

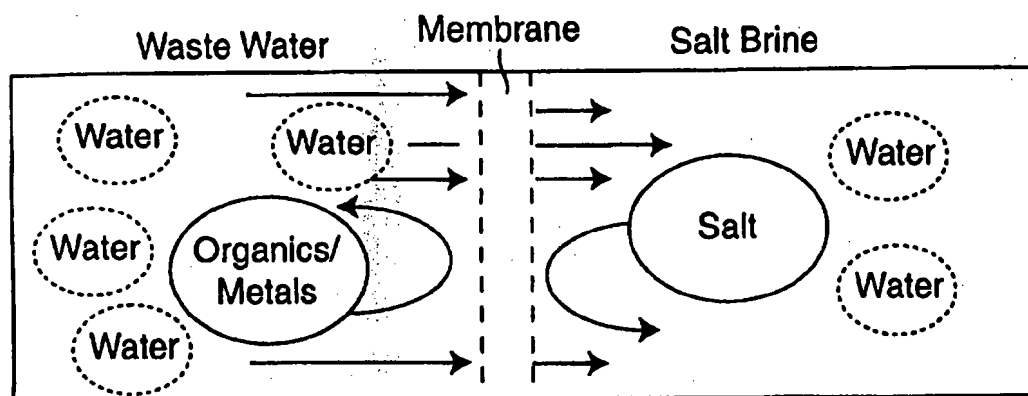


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(54) Title: DIRECT OSMOTIC CONCENTRATION CONTAMINATED WATER

Direct Osmosis



(57) Abstract

There is disclosed a method for recovering pure water from aqueous contaminated streams containing high levels of salts and suspended solids, such as landfill leachate, comprising (a) contacting the aqueous stream with one side of a semipermeable membrane, the other side of which is in contact with an aqueous brine solution at a higher osmotic pressure, wherein the aqueous stream is provided at a pressure less than 350 kPa, whereby pure water passes through the membrane from the aqueous stream into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) and electrodialysis process, (3) an evaporation process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution.

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DIRECT OSMOTIC CONCENTRATION CONTAMINATED WATER

TECHNICAL FIELD OF THE INVENTION

5 The present invention provides a process for direct osmotic concentration and processing for water recovery from highly contaminated streams. The process is especially well suited to situations where very high levels of water recovery are desired, and to streams which induce fouling in other processing technologies, such as streams with high salt and suspended solids, such as waste water, brackish water, and landfill leachate. High level
10 water recovery allows for incineration of the residual sludge.

BACKGROUND OF THE INVENTION

 There are numerous situations where the recovery of more than 95% of the water from "fouling prone" streams is required. A good example is the discharge of graywater
15 from ships in port (graywater includes shower, laundry, and galley water, but excludes sewage). Sewage is often called "blackwater." Previously, ships have simply discharged this water into the harbor, but with increasingly stringent regulations, this waste is often pumped to local sewage facilities. Sewer hookups are expensive and not always available so a method for storing the waste onboard while in coastal waters is desired. For this to be
20 feasible, however, a reduction of the waste water volume is desired.

 The composition of graywater makes a volume reduction difficult to accomplish by conventional means (e.g., reverse osmosis or evaporation). Graywater contains high levels of soap which causes rapid fouling in conventional systems, so that keeping systems in operation requires pretreatment of the waste and frequent equipment cleanings. In addition,
25 evaporation is very energy intensive, and reverse osmosis is not capable of high levels of water recovery. Graywater has been treated by electrodialysis at sea to obtain a concentrated salt brine. However, the process of electrodialysis is energy intensive and difficult to run at sea. Therefore, there is a need in the art to develop less energy-intensive and more efficient treatment methods for graywater recovery that can be used, for example,
30 at sea or in a space craft (e.g., space shuttle or space orbiter).

 Another situation requiring high levels of water recovery is desalination of brackish ground water in arid regions. In many areas with very low rainfall, the ground water becomes brackish by leaching salts from the soil. This water is often high in dissolved calcium and magnesium, which makes evaporative or electrodialytic desalination most
35 difficult. Reverse osmosis has been used, but is only capable of recovering a low percentage of the water (e.g., 40% to 80% of the water must be sewerred). A higher recovery of water is desired due to the limited quantity of ground water available. Moreover, there is a significant fouling problem when running RO on brackish water, necessitating a pre-filtration

procedure. Therefore, RO procedures (with or without pre-filtration) provides an inefficient and high cost procedure to obtain potable water. Therefore, there is a need in the art to greatly increase the efficiencies of brackish water reclamation into potable water for arid regions with only brackish water supplies available.

5 Further there is a treatment problem for landfill leachates and contaminated process streams from industrial operations of materials, such a wallboard, wherein the waste streams contain high concentrations of membrane-fouling suspended solids. With regard to landfill leachates, there are several states that require treatment of the landfill leachate as it can be classified as a hazardous material. Therefore, the options available for landfill leachate are
10 on site treatment or to transport the leachate, often copious quantities after rain, to off site treatment facilities, such as sewage treatment. The on-site treatment options include settling ponds and evaporation, but this is only workable in extremely arid climates, and a reverse osmosis technique. However, RO is prone to fouling. Moreover, those techniques that limit fouling are only able to remove at most 80% of water, which does not provide a necessary
15 economic solution to the leachate problem. Therefore, the present invention can provide the high concentrations of water removal from leachate, up to the 95-98% water removal range to provide an economical and effective solution to on site treatment of landfill leachate. The present inventive process and apparatus allows for recovery of high amounts of potable water and other solvent recovery while preventing membrane fouling.

20 Direct Osmosis Concentration (DOC) is a process in which osmosis is used to pull water from a solution (*i.e.*, feed or feed solution), through a semi-permeable membrane, into an Osmotic Agent solution (OA). The semi-permeable membrane is permeable to water, but essentially impermeable to other species. Osmotic transfer of water from the feed solution into the OA occurs because of the high concentrations of dissolved solids maintained in the
25 OA. This gives the OA a very high osmotic potential, causing it to pull water through the membrane from the feed.

For the process to operate on a continuous basis, a method for removing water from used OA is needed; water absorbed by the OA in the DOC process must subsequently be removed before the OA can be reused. Methods previously used to reconcentrate the OA
30 include; thermal evaporation, solar evaporation, reverse osmosis, and electrodialysis. In a thermal evaporator, water is boiled from the OA under vacuum. This is the most common method for reconcentrating sugar OAs, however it is less desirable for salt OAs because of corrosion problems associated with heated salt solutions. Thermal evaporation is also energy intensive; typically, about 750 BTU is used for every pound of water evaporated.

35 Solar evaporation is an attractive option in regions where the climate is favorable. In this scheme, diluted salt brine is introduced to an open pond or tank, and incoming solar energy causes the water to evaporate. Drawbacks to this option are the large tank area required, and the care needed to keep salt from leaking into the groundwater.

Reverse osmosis (RO) is an option for salt brine reconcentration because it requires less energy than evaporation. In RO, water is separated from a salt brine by applying sufficient pressure to the salt brine that water is forced from it through a semipermeable membrane. However, RO has a significant limitation in that an 8% salt concentration is the maximum attainable in conventional RO systems, whereas, in some cases, a 15-25% salt concentration is desired in DOC systems.

Electrodialysis (ED) is another membrane technology that can be used to reconstitute the salt brine. In ED, a portion of the salt brine is totally deionized by electrically pulling all salt from it through ion-selective membranes into the remainder of the salt brine. ED is capital intensive and requires significant amounts of electricity to run.

SUMMARY OF THE INVENTION

The present invention provides a method for recovering pure water from aqueous contaminated streams containing high levels of salts and suspended solids, comprising (a) contacting the aqueous stream with one side of a semipermeable membrane, the other side of which is in contact with an aqueous brine solution at a higher osmotic pressure, wherein the aqueous stream is provided at a pressure less than 350 kPa (e.g., 50 psi), whereby pure water passes through the membrane from the aqueous stream into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) an electrodialysis process, (3) an evaporation process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution. Preferably, the aqueous stream containing high levels of salts and suspended solids is selected from the group consisting of brackish water, surface water, well water, fish processing waste water, pulp and paper processing waste water, power plant discharge water, humidity condensate, sea water, and combinations thereof. Preferably, the aqueous stream has a fluid velocity across the membrane surface greater than 0.15 m/sec to help sweep away fouling materials before they lodge on the membrane surface. Preferably, the membrane is configured in a corrugated or tortuous flow design to augment turbulence.

Preferably, the salts include inorganic salts and organic salts. Preferably, the aqueous brine solution is a concentrated or saturated solution of a chloride salt, such as sodium chloride, potassium chloride or calcium chloride. Preferably, the aqueous brine solution is recycled and reused. Preferably, the recovering step is performed with RO to reconcentrate the aqueous brine solution.

The present invention further provides a method for treating graywater or filtered blackwater, comprising (a) contacting the graywater or filtered blackwater with one side of a semipermeable membrane, the other side of which is in contact with an aqueous concentrated salt brine solution at a higher osmotic pressure, wherein the graywater or filtered blackwater

is provided at a pressure less than 350 kPa (*e.g.*, 50 psi), whereby pure water passes through the membrane from the graywater or filtered blackwater into the concentrated salt brine solution to dilute the concentrated salt brine and form a sludge of concentrated graywater or filtered blackwater at less than 5% of its original volume, (b) disposing of the graywater or filtered blackwater sludge, and (c) discarding the diluted salt brine into the ocean. The graywater or filtered blackwater treatment process is an energy efficient process utilizing the osmotic potential of a concentrated salt brine solution instead of an energy source, whereby the concentrated brine solution would normally be generated in a ship at sea during its normal desalination processes for obtaining potable water. Moreover, the concentrated salt brine generated during desalination would not be discardable unless diluted with potable water. Preferably, the aqueous stream has a fluid velocity across the membrane surface greater than 0.15 m/sec to help sweep away fouling materials before they lodge on the membrane surface. Preferably, the membrane is configured in a corrugated or tortuous flow design to augment turbulence.

The present invention further provides a method for treating landfill leachate, comprising (a) contacting the leachate with one side of a semipermeable membrane, the other side of which is in contact with an aqueous brine solution at a higher osmotic pressure, wherein the leachate is provided at a pressure less than 350 kPa (*e.g.*, 50 psi), whereby pure water from the leachate passes through the membrane into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) an electrodialysis process, (3) an evaporation process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution. Preferably, the leachate has a fluid velocity across the membrane surface greater than 0.15 m/sec to help sweep away fouling materials before they lodge on the membrane surface. Preferably, the membrane is configured in a corrugated or tortuous flow design to augment turbulence. Preferably, the landfill leachate is pretreated by a process selected from the group consisting of ultrafiltration, reverse osmosis, and combinations thereof whereby the pretreatment process is able to remove up to 80% of the water in landfill leachate but is not able to remove the much higher concentrations of water as the inventive process.

Preferably, the salts include inorganic salts and organic salts. Preferably, the aqueous brine solution is a concentrated or saturated solution of a chloride salt, such as sodium chloride, potassium chloride or calcium chloride. Preferably, the aqueous brine solution is recycled and reused. Preferably, the recovering step is performed with RO to reconcentrate the aqueous brine solution.

Examples of commercial applications of the inventive process are for recycling graywater on ships, recovering and reusing waste water at car washes and laundromats, treatment of boiler feed streams at power plants, and other areas where the supply of clean

fresh water is limited. Additional applications are to utilize brackish water as a potable water supply in an economical and energy-saving manner.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Figure 1 shows a schematic diagram of the inventive DOC process.

Figure 2 shows that the flux rates are constant over time indicating the lack of fouling using the inventive method when the highly contaminated aqueous stream used was made from 73% shower water, 22% ersatz humidity condensate and 5% untreated urine.

10 Figure 3 shows a schematic of the inventive DOC process with an RO system to reconstitute the salt brine solution.

Figure 4 shows flux rates over time for graywater treatment using seawater as the OA/slat brine solution. These data indicate a lack of fouling using the inventive process.

15 Figure 5 shows the same experiment as Figure 4 (reported in example 1) only using a more highly concentrated salt brine solution of 7 wt% NaCl OA instead of seawater. Again, the flux rates over time indicate a lack of fouling using the inventive process.

Figure 6 illustrates a process flow diagram showing the inventive method.

Figure 7 illustrates a bench top version of a DOC device.

Figure 8 illustrates a schematic of mass balances for water recovery from the ersatz waste model described herein.

20 Figure 9 illustrates the water removal rate from the ersatz waste water and is representative of water permeation rate at a given fraction of water recovered. In Figure 9, flux rates are plotted as LMH versus an average of the fraction of water removed at the beginning and end of a sample interval. The flux rate decreased as the amount of water recovered increased. This was due to an increase in osmotic pressure of the waste solution as the solids became more concentrated.

25 Figure 10 illustrates the performance of chloride-containing salts. The upper panel shows the rate of water uptake versus the number molarity of the salt. The number molarity is the moles of ions, assuming complete dissociation of the salts, in a kg of water. The abscissa is the average of the beginning and ending samples for the time interval. The lower panel was the last series of runs, which indicated that there was a decline in membrane flux-performance during the initial screening tests. Figure 10 (lower panel) shows the kg of salt lost from the brine solution into tap water for each kg of water removed. The actual salt-loss rate was determined by multiplying by the flux rate of water removed. The salt-loss tended to be less than 0.1% of the water-removal rates.

35 Figure 11 illustrates the effect of the anion of DOC performance. The upper panel of Figure 11 assumes complete dissociation of the salts. If sodium citrate and sodium sulfate are assumed to have only one Na^+ dissociate, then they would lie on the same trend as sodium chloride and sodium acetate. Figure 11 shows the kg of salt lost from the brine

solution into the waste (tap water) for each kg of water removed. Sodium chloride exhibited the largest salt-loss rate for the sodium series, but it was less than 0.05% of the water removal rates.

Figure 12 illustrates a two-stage DOC system experimental set up. There were no back pressure valves used on the waste side because the waste tank was elevated, which provided a needed 7-14 kPa pressure differential between the waste and the brine solution. The feed (*i.e.*, waste) was fed into a first Stage as water diffused through the membrane into the brine solution. Water that diffused through a second stage membrane into the brine solution was automatically replaced by partially concentrated from Stage 1. The concentrated waste was manually withdrawn from Stage 2 at various times for analysis. The brine solution was set up to flow in a countercurrent to the waste flow.

Figure 13 illustrates an electrodialysis (ED) test system.

Figure 14 illustrates the mass balance for continuous processing of waste water.

Figure 15 illustrates water removal rates from actual composite waste water. Flux results are plotted in Figure 15. Flux declined by approximately 10% during a run, but this was due to feed strength of the brine solution dropping by about 20%.

DETAILED DESCRIPTION OF THE INVENTION

The present invention uses osmosis through a semipermeable membrane to provide a method for removing water from contaminated aqueous streams. The invention is capable of removing up to 98% of the water from highly contaminated feed streams that tend to cause rapid fouling of other membrane evaporation systems (*e.g.*, RO, evaporation, etc.). The invention is particularly useful in situations where a high level of water recovery is desired and the feed stream causes rapid fouling of other membrane or evaporation systems. In addition, the invention has the capability of processing fluids containing high levels of suspended solids with no pretreatment. Previously, the only commercial-scale method available to treatment of highly contaminated aqueous streams has been reverse osmosis (RO), which requires much higher operating pressures, necessitating the use of more expensive equipment to withstand such pressures and prevents the use of much cheaper molded plastic materials due to pressures used.

In the invention, direct osmosis is used to extract water from a contaminated stream by introducing the stream to one side of a semipermeable membrane and an "osmotic agent" (a solution with a higher osmotic potential, such as a salt brine solution) to the other side. Because of the difference in osmotic potential, water diffuses through the membrane from the feed into the osmotic agent. The structure of the membrane polymer allows the passage of water but blocks the movement of larger molecules, with the result that contaminants in the feed stream do not cross into the osmotic agent or concentrated salt brine solution. A schematic diagram of the process is shown in Figure 1.

Osmotic potential is a measure of how strongly a solution draws water through a semipermeable membrane. The phenomenon is caused by the presence of dissolved solids in the solution and the osmotic potential, π , is closely approximated by

$$\pi = cRT$$

- 5 where c is the molar concentration of dissolved species, R is a gas constant, and T is the absolute temperature. Due to dependence on molar concentration, low molecular weight dissolved species (*e.g.*, salts) have a much higher osmotic potential per unit weight than large species (*e.g.*, soaps).

- 10 The osmotic potential of most graywater is low since its largest dissolved component is soap. It is therefore possible to osmotically concentrate graywater to high levels with relatively weak salt solutions. In early attempts at the inventive process (see example 1), 97% of the water was extracted from a simulated combination of laundry, shower and dishwater streams with seawater as the osmotic agent (3.5 wt% brine). When a 7 wt% brine was used as the osmotic agent, 98.4% of the water was removed. A 7 wt% brine OA is
15 representative of the brines produced in typical desalination processes. A list of ingredients in the simulated graywater is shown below in Table 1.

- Osmotic agents used in the inventive process are preferably salt solutions. Such salt solutions or brines include but are not limited to solutions containing Na^+ , K^+ , Ca^{++} , Mg^{++} , Li^+ , Cl^- , SO_4^{--} , or organic anions such as ascorbate, citrates or large polyelectrolytes. The
20 osmotic agent, or salt brine solution can also be seawater or salt brines from industrial or desalination processes. Osmotic agent made from non-ionic solutions (*e.g.*, sugars) can be used, however the flux is slower than the flux for ionic species.

- Membranes used in the present invention are preferably highly hydrophilic and highly selective. Typical membrane materials are polyvinyl alcohol-derivatives and cellulose-based
25 polymers, such as cellulose acetate, cellulose triacetate, cellulose butyrate, and cellulose propionate. These membranes absorb water from the waste into the polymer matrix while rejecting larger molecules. The absorbed water diffuses through the polymer into the osmotic agent or salt brine solution. Water transfer rates increase with thinner membranes.

- Direct Osmosis Concentration (DOC) is used to concentrate a waste stream for
30 storage or processing, or it can be used as a "foulant-eliminating" pretreatment step in the desalination of water. An attractive feature of the invention is it can extract a much higher percentage of water from a solution than reverse osmosis. In reverse osmosis (RO), water is forced from a solution through a membrane by exerting high pressures on the fluid (up to 7 MPa, or 1000 psi). This pressure is needed to overcome the natural tendency for the water
35 in the membrane to diffuse back into the feed solution. Many common osmotic agents have extremely high osmotic potentials, for example a 15% NaCl solution has an osmotic potential of 16 MPa (2300 psi), so DOC can continue to extract water far past the point where RO reaches its upper concentration limit.

Another advantage of DOC is it avoids much fouling which plagues evaporators and RO systems. Fouling occurs in evaporators because evaporation on the hot heat-transfer surfaces tends to cause precipitation of fouling substances, which are subsequently "baked on" the surface. In reverse osmosis, the extremely high pressure gradients at the membrane surface (up to 1013 Pa/m or 4,000,000 psi/inch) also favor the formation of fouling layers. In DOC, however, the only fouling is that caused by adhesion of solute molecules to the membrane due to surface energy effects. Such fouling occurs slowly and can usually be avoided by using a hydrophilic membrane and instilling turbulence in the fluid at the membrane surface.

The absence of pressure and temperature gradients also enables the processing of streams containing high levels of suspended solids. For example, the DOC process is not impaired by the presence of particulates in graywater, or by calcium sulfate crystals in concentrated brackish ground water.

In general, the inventive process is attractive in four situations. The first is instances where a waste needs to be concentrated, and an existing source of brine is available. An example of this is shipboard concentration of graywater. In this application, sea water or brine from the ship's desalination system is be used as the brine solution. Since the brine does not need to be reconcentrated after absorbing water, the waste concentration requires less energy consumption than evaporation or reverse osmosis. The second situation occurs when a waste needs to be concentrated and fouling makes other technologies inappropriate. An example of this is removal of water from chemical process solutions before incineration. In this case, the water absorbed by the brine is often removed by evaporation so the brine is reused. Thirdly, the present inventive process is most useful for on site treatment of landfill leachate. The inventive process can remove about 95% or even greater concentrations of potable water from even hazardous leachates, whereas RO systems can effectively remove only about 80% of water reliably from leachates with high suspended solids concentrations. The inventive process involves a high degree of portability and does not require significant use of electricity to drive high pressure pumps (as in RO processes) thus providing an energy efficient solution to landfill leachate problems. Lastly, the invention is attractive as a pretreatment to remove foulants from a stream before desalination. In cases where the water source has extremely high hardness, DOC is used to produce a stream of higher salinity but lower hardness. The low hardness stream is desalinated by electrodialysis, reverse osmosis, or evaporation. The removal of potable water also reconcentrates the brine for reuse. An example of this is the recovery of high levels of water from brackish water in arid regions.

The inventive process is distinct from prior art water recovery processes because of high levels of water recovery and a resistance to membrane fouling. Figure 2 shows the water flux from graywater when the osmotic agent and product concentrations are held

constant. This demonstrates that the inventive process is not subject to fouling induced flux declines experienced by other membrane processes when processing graywater.

There are three important parameters of the inventive process that distinguish the present invention from RO and earlier attempts at DOC concentration techniques and provide the lack of fouling advantage and the economic advantages of the inventive process. The first requirement is low pressure, particularly having the feed pressure be lower than 350 kPa (about 50 psi), preferably lower than 140 kPa (20 psi). Other membrane processes, such as RO, operate above 400 psi, which induce rapid formation of fouling layers on the membrane. Moreover, a system operating at such low pressures can be made from molded plastics allowing for much less expensive designs and reduced capital costs due to the need for less expensive pumps that only operate at lower pressures. Secondly, the fluid velocity is preferably pumped across the membrane surface at velocities above 0.15 m/sec. This motion helps sweep away fouling prone materials before they lodge on the membrane surface. Further the cell design, preferably, has a tortuous or corrugated flow path, such as the design described in U.S. Patent 5,281,430, the disclosure of which is incorporated by reference herein.

Osmotic agents (OA) or aqueous brine solutions used herein preferably are available (e.g., seawater) or continuously reconcentrated. Methods for reconcentrating the aqueous brine solution include, for example, RO, evaporation, electrodialysis, and combinations thereof. A preferred scheme is shown in Figure 3.

The present invention provides a method for recovering pure water from aqueous contaminated streams containing high levels of salts and suspended solids, comprising (a) contacting the aqueous stream with one side of a semipermeable membrane, the other side of which is in contact with an aqueous brine solution at a higher osmotic pressure, wherein the aqueous stream is provided at a pressure less than 350 kPa (e.g., 50 psi), whereby pure water passes through the membrane from the aqueous stream into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) an electrodialysis process, (3) an evaporation process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution. Preferably, the aqueous stream containing high levels of salts and suspended solids is selected from the group consisting of brackish water, surface water, well water, fish processing waste water, pulp and paper processing waste water, power plant discharge water, humidity condensate, sea water, and combinations thereof. Preferably, the aqueous stream has a fluid velocity across the membrane surface greater than 0.15 m/sec to help sweep away fouling materials before they lodge on the membrane surface. Preferably, the membrane is configured in a corrugated or tortuous flow design to augment turbulence.

Preferably, the salts include inorganic salts and organic salts. Preferably, the aqueous brine solution is a concentrated or saturated solution of a chloride salt, such as sodium chloride, potassium chloride or calcium chloride. Preferably, the aqueous brine solution is recycled and reused. Preferably, the recovering step is performed with RO to reconcentrate the aqueous brine solution.

The present invention further provides a method for treating graywater or filtered blackwater, comprising (a) contacting the graywater or filtered blackwater with one side of a semipermeable membrane, the other side of which is in contact with a concentrated aqueous brine solution at a higher osmotic pressure, wherein the graywater or filtered blackwater is provided at a pressure less than 350 kPa (e.g., 50 psi), whereby pure water passes through the membrane from the graywater or filtered blackwater into the concentrated aqueous brine solution to dilute the concentrated aqueous brine and form a sludge of concentrated graywater or filtered blackwater at less than 5% of its original volume, (b) disposing of the graywater or filtered blackwater sludge, and (c) discarding the diluted aqueous brine into the ocean. The graywater or filtered blackwater treatment process is an energy efficient process utilizing the osmotic potential of a concentrated aqueous brine solution instead of an energy source, whereby the concentrated aqueous brine solution would normally be generated in a ship at sea during its normal desalination processes for obtaining potable water. Moreover, the concentrated aqueous brine generated during desalination would not be discardable unless diluted with potable water. Preferably, the aqueous stream has a fluid velocity across the membrane surface greater than 0.15 m/sec to help sweep away fouling materials before they lodge on the membrane surface. Preferably, the membrane is configured in a corrugated or tortuous flow design to augment turbulence.

Examples of commercial applications of the inventive process are for recycling graywater on ships, recovering and reusing waste water at car washes and laundromats, treatment of boiler feed streams at power plants, and other areas where the supply of clean fresh water is limited. Additional applications are to utilize brackish water as a potable water supply in an economical and energy-saving manner.

The inventive process, as applied to graywater on a ship at sea, also avoids the high cost of electrodialysis, providing that RO is used for the recovering step. The inventive process recovers over 98% of the water from most sources containing high levels of salts (e.g., calcium and magnesium hardness, bicarbonates/alkalinity, barium or strontium sulfate, fluorides, chlorides, silica, iron, and organics, including long chain hydrocarbons). The process is suitable for zero or minimum discharge operations in the treatment of municipal or industrial waste waters. Moreover, the inventive process provides a more economical, or in some cases, an only alternative for treatment of waste waters containing high levels of suspended solids. For example, the inventive process is suitable for boiler feed water pretreatment, specifically at those sites where high levels of silica in the raw water could

hinder the performance of high pressure boilers in the electric power industry. Treatment of high silica water by conventional RO techniques, results in a high degree of membrane fouling and extremely short membrane lives.

In direct osmosis concentration, water was extracted from a brackish solution through a membrane into a brine solution. The mechanism driving the process was simple diffusion, water moved through the membrane into the brine solution because the brine solution was more concentrated than the brackish water. The membrane had rejection characteristics such that water passed freely while salt rejection was very high. The advantage of this process was the calcium and magnesium salts that make desalination of the brackish water difficult were isolated in the feed stream concentrated to 10% of its original volume. Potable water was extracted from the brine solution. Up to 90% of the water was recovered from the brackish feed stream.

Membranes used in the invention are preferably hydrophilic and have molecular selectivity's similar to those of reverse osmosis membranes. Examples of such membranes are cellulose-based asymmetric membranes and hydrophilic thin-film composite membranes. Membrane configurations which may be used for DOC, include, but are not limited to, hollow fiber, spiral wound, plate-and-frame and tubular. Plate-and-frame and tubular configurations are preferable in many applications as they are more tolerant of high levels of suspended solids.

Aqueous brine solutions useful in the process include but are not limited to inorganic and organic salt solutions, sugar solutions, and polyelectrolyte solutions. The selection of the aqueous brine solution is determined by solubility's, osmotic strength of solutions, permeability of the osmotic agent through the membrane, and economics. In general, an effective osmotic agent (OA) or aqueous brine solution has high diffusivity, high solubility, and low molecular weight of the dissolved species. High diffusivity is desirable because water being drawn through the membrane tends to sweep the OA salts away from the membrane surface. This reduces the brine strength at the surface, and reduces the water removal rate. A high diffusivity quickly replenishes the aqueous brine salts at the surface.

High solubility and low molecular weight of the dissolved salts in the aqueous brine solution are desirable because the osmotic potential of the solution is roughly proportional to the number density of dissolved molecules. As a result, a light, highly soluble salt such as sodium chloride gives the fastest water removal rates.

In cases where it is critical that the feed solution not be contaminated by salt from the osmotic agent, sugar and polyelectrolyte solutions may be used as the osmotic agent. Salt contamination can occur because DOC membranes are not 100% impermeable to light salts. For example, when a sodium chloride osmotic agent and a cellulose triacetate membrane are used, approximately 0.1 to 1.0 mg of salt crosses from the osmotic agent into the feed for every kilogram of water extracted. DOC membranes completely block larger species such as

sugars and polyelectrolytes. However osmotic agents using these larger species of OA deliver lower fluxes than those obtained with light salts.

The inventive method was tested with a variety of aqueous streams containing high levels of salts and suspended solids to recover essentially pure water. The first step of the inventive process is a direct osmotic concentration (DOC) of the aqueous stream. In the DOC step, water is recovered from the contaminated aqueous stream by placing the aqueous stream and a clean, concentrated aqueous brine solution on opposite sides of a membrane. The membrane is, preferably, a semipermeable membrane, allowing water passage and rejecting the passage of all but the smallest compounds. The concentrated salt solution is called an aqueous brine solution because it has a higher osmotic potential than the aqueous stream. For example, a 15 weight percent NaCl solution as an aqueous brine solution has an osmotic potential of 16 MPa (2300 psi). The DOC process step is nonfouling (irrespective of the level of suspended solids present in the aqueous stream) because there are no large gradients established by external forces. Water is removed from the aqueous stream using only diffusion, driven by an osmotic gradient. Water naturally diffuses from the aqueous solution into the concentrated brine solution, concentrating the aqueous stream and diluting the brine solution. The diffusion of water will continue until the osmotic potentials of the concentrated aqueous stream and diluted aqueous brine solution are the same.

The clean, diluted aqueous brine solution is reconstituted in the second step to yield recovered potable water and concentrated salt solution as reusable aqueous brine solution. This reconstitution step can be accomplished by evaporation, electrodialysis, RO, and combinations thereof. When electrodialysis was used for the reconstitution step, a process flow diagram shows the inventive method in Figure 6. Therefore, the aqueous brine solution essentially acts as a carrier for clean, potable water. As shown in Figure 6, the regenerated concentrated aqueous brine solution is recycled to act as the OA or aqueous brine solution. The use of DOC (direct osmotic concentration) provides advantages because no pretreatment of waste is required, no large temperature gradients (*i.e.*, evaporators) are needed, and no large pressure gradients are needed, such as those needed in reverse osmosis. No phase changes occur with DOC and low pumping pressures are needed. Moreover, since reverse osmosis membranes are, preferably, used for the DOC step, microbial contamination is prevented from reaching the final potable water product.

Preferably, the aqueous brine solution is a concentrated or saturated solution of a chloride salt, such as sodium chloride, potassium chloride or calcium chloride. Preferably, the aqueous brine solution is recycled and reused. Figure 10 shows the performance of chloride-containing salts. The upper panel shows the rate of water uptake versus the number molarity of the salt. The number molarity is the moles of ions, assuming complete dissociation of the salts, in a kg of water. For concentrated salt solutions, the osmotic potential of the OA is proportional to the number molarity ($\pi = m_n \rho_w RT$). The abscissa is

the average of the beginning and ending samples for the time interval. The lower NaCl curve was the last series of runs, which indicated that there was a decline in membrane flux-performance during the initial screening tests. Figure 10 (lower panel) shows the kg of salt lost from the aqueous brine solution into tap water for each kg of water removed. The actual salt-loss rate was determined by multiplying by the flux rate of water removed. The salt-loss tended to be less than 0.1% of the water-removal rates. A solution-diffusion model for reverse osmosis (RO), as applied to DOC, predicts that the salt-loss ratio should be constant for solutions of a single salt. The salt-loss ratio for NaCl was approximately constant.

The relative size of the cations in solution at infinite dilution is $K^+ < Na^+ < Li^+ < Ca^{++}$. For a fixed anion, the larger the cation, the greater the membrane rejection of the salt. When mass transfer rates in an asymmetric, porous layer of the membrane are important, the smaller the ion, the faster its diffusion rate, which leads to higher water fluxes. We observed this trend, although LiCl appeared to have higher water fluxes. The equivalent molality (equivalents per kg of water) was used to compare aqueous brine solutions for a DOC/ED process (as opposed to number molarity), because electrodialysis was used to reconstitute the aqueous brine solution in this example. A $CaCl_2$ brine solution would require 1.5 times more energy to reconstitute by ED than the 1:1 salts. Therefore, univalent salts are preferred for the aqueous brine solution.

Preferably, the recovering step is performed with reverse osmosis (RO) as more economical than electrodialysis, or the recovering step is performed with both RO and electrodialysis.

Example 1

This example illustrates the preparation of an ersatz waste stream that was used as a model for testing treatment of gray water. The composition of this model gray water approximated the salt levels, TOC (total organic carbon), and major chemical constituents of a combination of urine and shower, hygiene and laundry waste water. The components are listed in Table 1.

Table 1 Composition of Ersatz Waste Water

	<u>Concentration mg/l</u>	<u>TOC mg/l</u>
<u>Inorganics</u>		
NaCl	565	
KCl	116	
K_3PO_4	16	
K_2SO_4	227	
$Ca_2(PO_4)_2$	4	
$MgSO_4$	70	

Organics

Urea	971	194
Ammonium Citrate	308	98
Creatinine	106	45
Histidine	124	57
Lactic Acid	174	69
Acetic Acid	110	44
Sebacic Acid	93	55
Caprylic Acid	71	47
SDBS (laundry soap)	33	21
<u>6503.45.4 (shower soap)</u>	<u>719</u>	<u>72</u>
total	3733	708

An actual waste water stream was further composed of 72.8% by volume shower, hygiene and laundry water (obtained from Umpqua Research Company (Myrtle Creek, OR)), 21.7% humidity condensate (made by diluting one part ersatz condensate concentrate (Umpqua) with nine parts of distilled water), and 5.5% untreated urine from a male
 5 volunteer. The analysis of this waste water stream was 525 mg/l TOC, 184 mg/l Na⁺, 259 mg/l K⁺, 7.33 mg/l Ca⁺⁺, and 4.71 mg/l Mg⁺⁺.

The graywater of Table 1 was concentrated as a 30 liter batch in a laboratory-scale cell having a membrane area of 0.07 m². Sodium chloride brines were used and brine concentrations were maintained by adding salt to the brine tank. Figures showing flux versus
 10 time and percent recovery are provided in Figures 4 and 5, respectively. Membranes used were asymmetric cellulose triacetate membranes cast by immersion precipitation on a net backing. Total membrane thickness was 170 microns. The membranes had selectivities similar to those of reverse osmosis membranes and the biological oxygen demand of water passing through the membrane was measured to be less than 1 ppm in each run.

15

Example 2

This example describes an experiment to evaluate several membranes within a bench-top DOC device to determine flux rates and performance criteria for several membranes. The DOC device is described in United States Patent 5,281,430, the disclosure of which is
 20 incorporated by reference herein. The bench top version of this device is illustrated in Figure 7. The waste water was sandwiched between a pair of membranes which separate the waste from the aqueous brine solution, which flows in the end plates. The membranes and plates can be stacked like plate-and-frame heat exchangers, however in this experiment, only one pair of membranes was used. The cell dimensions were 0.30 x 0.23 x 0.06 m and each
 25 membrane was 0.28 x 0.20 m. The effective transfer area was approximately 0.23 x 0.15 m or about 0.07 m² for the two membranes. The cell was plumbed with all necessary valves,

gauges and tubing, and leak tested. The membranes tested included cellulose triacetate (backed and unbacked) (Purification Products), cellulose acetate (Purification Products), Nafion® 112 (DuPont), and SW-30 aromatic polyamide (FilmTec).

The initial membrane screenings were done with a 13 to 15 weight percent NaCl solution as the brine solution and either tap water or dilute corn syrup as the waste. Flux rates were determined by measuring the change in volume of the tap water. The amount of salt lost into the waste was determined by measuring conductivity of the tap water or diluted corn syrup and then accounting for the measured change in the amount of the waste. Table 2 shows the results from initial screenings with tap water. The Nafion® membrane was not tested with tap water as the waste, however when corn syrup was used, Nafion® performed just as poorly as the SW-30 membrane. Flux rates are shown in LMH (liters of water removed per square meter of effective membrane area per hour). Salt-loss ratio estimates are how many kg of salt are transferred from the brine solution into waste for every kg of water diffusing in the opposite direction (*i.e.*, from waste into the brine solution).

Table 2 Initial Membrane Screening Results		
Membrane	Flux Rate LMH	Salt-Loss Ratio
cellulose triacetate	25.0	0.04%
cellulose triacetate backing 2	11.0	0.04%
cellulose triacetate (factory backed)	14.4	0.13%
cellulose acetate	14.5	0.23
cellulose acetate (factory backed)	5.9	0.19%
SW-30	1.9	0.06%

These data show that the unbacked cellulose triacetate membrane provided necessary high water flux rates and rejections necessary for the DOC system. The higher the flux, the smaller the required DOC equipment to recover water. Backing was added to this membrane to improve durability but not affect flux.

The unbacked cellulose triacetate (CTA) membrane was also tested with ersatz waste water described in Table 1 in example 1. A summary of mass balances are shown in the schematic in Figure 8. Generally, the brine solution was 3.0 liters of 15% NaCl by weight, diluted to 5-6 liters, then replaced. Over 97% of the water was recovered from ersatz waste. Figure 9 is representative of water permeation rate at a given fraction of water recovered. In Figure 9, flux rates are plotted as LMH versus an average of the fraction of water removed at the beginning and end of a sample interval. The flux rate decreased as the amount of water recovered increased. This was due to an increase in osmotic pressure of the waste solution as the solids became more concentrated. There was no evidence of membrane fouling during processing of ersatz waste water.

TOC was measured in the brine solution to determine how well organic compounds were being rejected by the membrane. The membrane rejected about 75% of the TOC present in ersatz water while recovering 97% of the initial water. This is a surprising result because over 30% of the TOC was from urea and acetic acid, compounds with molecular weights of 60 and are not well rejected by membranes as are the larger organic compounds.

Example 3

This example reports an experiment to evaluate the merits of various brine solutions for waste water treatment. Seven soluble salts were selected for incorporation as the brine solution, including NaCl, LiCl, KCl and CaCl₂ for cation effects and Na₂SO₄, NaC₂H₃O₂ (sodium acetate), and Na₃C₆H₅O₇ (sodium citrate) for anion effects. Tap water, CTA membranes and 15% by weight salts were used for salt comparisons. The DOC setup was the same used in example 2 above. Rejection rate of salt by the membrane was determined by measuring conductivity change due to concentrating water so that salt rejection rate of the membrane could be calculated.

The performance of the sodium series of brine solution salts is shown in Figure 11. The lower NaCl data points were the last run. The upper panel of Figure 11 assumes complete dissociation of the salts. If sodium citrate and sodium sulfate are assumed to have only one Na⁺ dissociate, then they would lie on the same trend as sodium chloride and sodium acetate. Figure 11 shows the kg of salt lost from the brine solution into the waste (tap water) for each kg of water removed. Sodium chloride exhibited the largest salt-loss rate for the sodium series, but it was less than 0.05% of the water removal rates. Its ratio was the largest because chloride is the smallest solvated anion of the series: chloride < sulfate < acetate < citrate. Preferably, sodium chloride is a desirable brine solution because of its solubility, it is strongly rejected by the membrane, suitable for electrodialysis recovery, nontoxic at low levels, and the anion and cation are each soluble with most of the contaminants that may get into the brine solution.

Example 4

This example presents the results of integrated testing of a DOC/ED process. A CTA membrane and a sodium chloride osmotic agent were used. A two-Stage DOC system was set up, as shown in Figure 12. There were no back pressure valves used on the waste side because the waste tank was elevated, which provided a needed 7-14 kPa pressure differential between the waste and the brine solution. The feed (*i.e.*, waste) was fed into a first Stage as water diffused through the membrane into the brine solution. The waste was fed into a first Stage (Figure 12) as water diffused through the a first Stage membrane into the brine solution. Water that diffused through a second stage membrane into the brine solution was automatically replaced by partially concentrated waste from Stage 1. The

concentrated waste was manually withdrawn from Stage 2 at various times for analysis. The brine solution was set up to flow countercurrent to the waste flow. The NaCl concentration in Stage 1 was 4-5 wt% and in Stage 2 was 6-8 wt%.

This experiment used an Ionics Mark I electrodialysis stack with a setup shown in Figure 13. The anode was platinum-coated titanium and the cathode was stainless steel. Two different power supplies were used, a Miller XMT-300CC DC Inverter Arc Welder for constant-amp currents above 6 A, and an ACDC Electronics Power Supply (Model OEM24N5.4-9) that delivered approximately 30 W with a maximum voltage of 22 v. The following membranes were used in the ED stack: cation-61-AZL-389 (Ionics) a cation-permeable membrane to isolate the electrode-rinse solutions, cation-64-LMP-401 (Ionics), and anion-204-UZL-386 (Ionics). The membranes were rated to handle the high concentrations of salts that were produced by regeneration of the brine solution.

Over 97% of the water was recovered from actual composite waste water using the foregoing DOC/ED process. The system was started with 3.0 liters of untreated waste water. As water was drawn into the brine solution, waste was fed into Stage 1 until the composition in Stage 2 corresponded to 97% volume recovered, which approximated the volume of water recovered. For a Stage 2 volume of 34 liters, this corresponded to approximately 12 liters of water passing through the membranes. During the initial startup, the 6.0 liters of 15% brine solution had removed 12 liters of water. Continuous processing began using different flow rates. There was 0.03 liters of concentrated waste withdrawn for each 1.03 liters of waste feed. For each 1.03 liters of waste feed, 1.45 liters (or 1.50 kg) of aqueous brine solution was removed from Stage 1, and 0.45 (or 0.50 kg) of 15 wt% NaCl was fed to the aqueous brine solution of Stage 2. This set the countercurrent flow rate at 0.5 kg of 15% NaCl per kg of water recovered. This system was run over a period of nine days and averaged 1 liter of potable water recovered per hour. At the end of each day, the fluids were drained and saved for the next day. The waste side was stored in dilute waste so as to avoid drying out the membranes.

Flux results are plotted in Figure 15. Flux declined by approximately 10% during a run, but this was due to osmotic strength of the aqueous brine solution dropping by about 20%. The final 3 days had concentrations of about 12 wt% NaCl. Approximately 20% of the membrane for Stage 2 was covered with a precipitate at the end of the 9 days. This precipitate was removed by a simple flush with unconcentrated hygiene water. No precipitate was formed on the Stage 1 membrane.

Initially, 15 kg of 15 wt% NaCl were made. A total of 26 kg of aqueous brine solution was needed to recover 52 liters of water, so a portion of the aqueous brine solution was reconcentrated in the ED. The ED stack was run in batches. Approximately 1 volume per membrane pair was required to achieve the required separations at higher concentrations. The energy requirements for producing deionized water and the reconstituted aqueous brine

solution in three steps are shown in Table 3 below. Most of the energy was used at the start, although the energy required to extract the last kg of salt is high, the overall effect is small. The DOC process requires little energy, approximately 1.4 watts per kg of water recovered.

Table 3

Δt min	Amps	volts	total ED, W	diluant l mg/l NaCl	W/kg NaCl	avg W/kg	kg H ₂ O recover ed	total W/kg H ₂ O
0				5.6	39,000			
70	9.5	10.8	103.0	5.1	14,000	820	820	3.1
0				4.1	14,000			3.1
113	2.9	8.3	24.5	3.9	800	850	830	3.1
0				8.8	800			3.1
50	0.7	21.7	15.6	8.7	80	2050	870	8.3
57	0.2	22.0	4.8	8.7	20	8810	880	8.3

- 5 The total ED power includes pumping energy of 0.45 W, calculated as: pumping pressure = 30 kPa (= 4.4 psig). (0.3 lpm diluant + 0.4 lpm concentrate + 0.2 lpm electrode rinse)/(60 s/min) x 30 kPa = 0.45 W (1 gpm = 3.785 lpm). The energy used by the lab-scale DOC to recover water with a waste-side inlet pressure = 17 kPa and a brine-side inlet pressure = 3.4 kPa was [(1.7 lpm waste x 17 kPa) + (4.1 lpm brine x 3.4 kPa)]/(60 s/min) = 0.7 W/stage.
- 10 (0.7 W/stage) x 2 stages/(1 kg H₂O recovered/hr) = 1.4 W/kg H₂O recovered. The total energy used by the lab-scale process (DOC/ED) to recover water was: 55.8 W/kg H₂O for ED + 1.4 W/kg H₂O for DOC = 57 W/kg H₂O recovered.

- A summary of the recovered water composition is shown in Table 4 below. TOC concentrations of the concentrate produced in ED were the same as deionized water. This means that TOC levels were not due to dissociated organic compounds, because they would have partitioned during ED. Initially we had 525 mg/l TOC, so the rejection of TOC was 70%. Further analysis showed that most of the TOC in recovered water was from urea, while the membrane rejected most of the other organics.

Table 4

Analysis	Composition of Recovered Water	
	Composite Waste Water	Urine
TOC mg/l	160	1490
Urea mg/l	628	6539
(Urea TOC)/TOC	78.5%	87.8%
pH	7.5	7.5
Conductivity, μ S/cm	80	350
Na ⁺ , mg/l	7.2	32.5
K ⁺ , mg/l	<0.02	0.86
Ca ⁺⁺ mg/l	0.118	0.39

Mg ⁺⁺ mg/l	<0.01	0.16
Cl ⁻ mg/l	12.1	not measured
SO ₄ ⁼ mg/l	<1	not measured
PO ₄ ⁼ mg/l	<0.01	0.052
NO ₃ ⁻ +NO ₂ ⁻ mg/l	<0.1	0.037

Over 90% of water was recovered from urine when treated in a batch mode designed to mimic countercurrent DOC operation. A single 0.07 m² DOC module (Stage 2) was used to recover 3.7 l of water from 4.2 l of urine in 13 hr. The mass balance for this run is described in Figure 16. The same membranes that were used for processing composite waste were also used for urine processing. Four and one tenth liters of 7 wt% NaCl were used as the brine solution. NaCl was added to the brine solution as the urine was concentrated to increase the driving force. The final concentration of brine solution was 14.5 wt% NaCl.

Water recovery rates are shown in Figure 17 and the analysis of recovered water is shown in Table 4. The water was not deionized to less than 100 µS/cm because (1) the system was operated in a batch mode with a final salt concentration of 14.5 wt% (the concentrate can only be made to about 15-16 wt% with the bulk of the water ending up in the concentrate with diluant running out), and (2) there was sodium aluminosilicate present in the initial salt, which was too large to diffuse through the ED membranes. In a continuous run, these issues can be overcome without undue experimentation, with a better salt source to achieve deionization levels of less than 100 µS/cm.

Example 5

This example illustrates a system requirement for an enclosed module (vehicle, space shuttle, etc.) with a four person crew. Larger or smaller modules will have their system designs adjusted proportionately. Assuming 97% recovery of waste water and 31.5 l per person per day (combination of laundry/shower/hygiene water, humidity condensate, and untreated urine), 18 hr of operation per day, the basic DOC system is two 0.5 m² modules in series with continuous dilute feed, 0.3 x 0.23 x 0.15 m per module and four peristaltic pump heads plus a drive with each capable of 12 lpm at 20 kPa. The basic ED system is three modules in series with 0.5-, 0.5-, and 0.25 m² effective membrane area with a physical dimension of 0.3 x 0.23 x 0.23 m for each 0.5 m² stage and 0.3 x 0.23 x 0.18 m for the 0.25 m² stage, plus six peristaltic pump heads plus a drive, each capable of 1 lpm at 30 kPa, and one 30 v DC power supply with 400 W output. The energy requirements are 24 W for DOC pumping, 3 W for ED pumping and 400 W for ED DC power for a total of 427 W/(6.8 l/hr), which is 63 W/kg water recovered.

Example 6

This example illustrates an experiment to determine if potable water can be obtained from a brackish ground water yielding high percent recoveries by using direct osmosis concentration (DOC), and to estimate costs of water production from a specified feed stream using this method. DOC is not a "stand alone" technology in this application, but is used in conjunction with ion-exchange, and electrodialysis or evaporation. The DOC process could also be used as a pretreatment to control the problems presented by the high levels of calcium and magnesium in the water. This experiment evaluated the DOC portion of the process only. The secondary technologies, electrodialysis of sodium chloride and ion exchange are known and their performance and cost can be easily determined.

High quality potable water was produced from brackish ground water by coupling DOC with electrodialysis.

Pilot Size:	4 gpm
Estimated Capital Cost:	\$180,000
Energy usage:	0.15 kW/kg H ₂ O
Water hardness:	<10 ppm
Water Recovery:	90%
By-product:	30 kg/day CaSO ₄ (gypsum)

For larger scale operations, the electrodialysis step can be replaced with a multiple effect evaporator.

Large System:	1000 gpm
Estimated Capital Cost:	\$10,000,000
Energy Usage:	600 kJ/kg H ₂ O (250 BTU/lb)
Water Hardness:	<10 ppm
Water Recovery:	90%
By-product:	7,500 kg/day gypsum

An ersatz brackish ground water was made from the following recipe:

H ₂ O:	60 kg
CaCl ₂ • 2H ₂ O	239 g
Na ₂ SO ₄	206 g
NaCl	353 g
MgCl • 6H ₂ O	231 g

Run #1: An initial concentration of the brackish water was made in a large pilot cell:

Membrane Area:	1.4 m ²
Test Duration:	3 hrs.
Temperature:	100 °F
Water Transferred:	45 L (75% recovery)
Initial NaCl Brine Conc.:	16%

Final NaCl Brine Conc.: 8%
 Hardness of Transferred Water: 290 ppm

Run #2: A further run was made in a smaller cell with the brackish concentrate from the first run.

5 Membrane Area: 0.33 m²
 Test Duration: 3 hrs
 Temperature: 100 °F
 Water Transferred: 71 (87% recovery)
 Initial NaCl Brine Conc.: 26%
 10 Final NaCl Brine Conc.: 18%
 Hardness of Water Transferred: Not Measured
 Observations: CaSO₄ in filter

Run #3: The small cell was run on the following morning and the water extraction rates were identical to those of Run #2 the previous day.

15 Conclusions:

1) No fouling of the membranes occurred. The flux (water extracted/hour/m² membrane) did not decline with time. In this application membranes can be expected to last over one year. Replacement membrane costs are around \$40/m².

20 2) If the temperature of the run is lowered to 70 °F, the hardness of transferred water is 100 ppm. This hardness must be removed or it will build-up during repeated cycles of the brine. At this level it is economically extracted by ion exchange.

3) In a staged system, if 90% recoveries are obtained and the brine enters the system at 15% and exits at 8%, the flux at 70 °F is 7 liters/hour/m² (LMH).

25 4) A relatively pure gypsum precipitates from the brackish water and can be sold as a by-product. Filtering a small side stream from the brackish water recirculation loop is enough to prevent the precipitate from lodging in the DOC cells.

5) A rough estimate of the cost of water from the pilot system is \$0.028/gal. This assumes electric costs of \$0.05/kWh. The cost from the large scale system is \$0.015/gal. No estimate of the value of the gypsum has been made.

30 The particular water sample tested, due to the high levels of Mg and Ca, was difficult to treat with other methods and was especially difficult to get the desirable high yields.

Example 7

35 This example illustrates laboratory testing for sizing a pilot-scale apparatus performing the inventive DOC process to provide on-site treatment of landfill leachate at a landfill site. A pilot scale DOC system described in U.S. Patent 5,281,430, the disclosure of which is incorporated by reference herein, was installed at a large regional landfill in Benton County, Oregon. The landfill was using a pretreatment system of chemical addition, settling,

- and microfiltration (0.2 micron membrane) to clarify the feed and then RO to concentrate the leachate because the RO system would be fouled quickly without initial pretreatment. This pretreatment, followed by RO, was able to remove from 78% to 83% of the water. A sample of the initially "concentrated" (pretreatment & RO) leachate was provided to the
- 5 DOC system as the feed for further concentration that could not be accomplished by the previous conventional means. The trial also proved the ability of the DOC apparatus using the inventive method to achieve concentrations of over 95% water removed.

- In one run, an attempt was made to quantify the amount of water DOC can remove from preconcentrated landfill leachate. The table below lists the elapsed time, volume of
- 10 feed, change in volume, total volume removed, membrane surface area and the flux achieved. The starting landfill leachate feed had been preconcentrated to have 80% of its water removed by an RO with pretreatment process. The osmotic agent (OA) used was a saturated aqueous NaCl solution. The feed was originally provided at 55 kPa (8 psi) but there was some foaming, so the feed pressure was reduced to 40 kPa (6 psi).

Elapsed time (hr)	Tank vol. (liters)	Vol. change (liters) from previous	Total vol. (liters)	area (m ²)	flux (LMH)
0:00	10.00	0.00	11.25	0.33	0
2:00	4.80	5.20	6.05	0.33	7.879
3:13	2.00	2.80	3.25	0.33	7.509
3:25	1.75	0.25	3.00	0.33	6.313
3:58	1.25	0.50	2.50	0.33	4.545

- 15 Over almost 4 hours of elapsed time, the 11.25 l sample of preconcentrated landfill leachate had been reduced to 2.5 l of sludge for an additional 78% volume reduction on top of the 80% reduction accomplished by the RO with pretreatment. The combination RO with pretreatment and DOC process reduced the volume of the original leachate to 95.56%. The overall flux rate for the DOC process was 7.406 LMH.

What is claimed is:

1. A method for recovering pure water from aqueous contaminated streams containing high levels of salts and suspended solids, comprising (a) contacting the aqueous stream with one side of a semipermeable membrane, the other side of which is in contact
5 with an aqueous brine solution at a higher osmotic pressure, wherein the aqueous stream is provided at a pressure less than 350 kPa, whereby pure water passes through the membrane from the aqueous stream into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) an electrodialysis process, (3) an evaporation
10 process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution.
2. The method of claim 1 wherein the aqueous stream containing high levels of salts and suspended solids is selected from the group consisting of brackish water, surface water, well water, fish processing waste water, pulp and paper processing waste water, power plant discharge water, humidity condensate, sea water, and combinations thereof.
- 15 3. The method of claim 1 wherein the aqueous stream has a fluid velocity across membrane surface greater than 0.15 m/sec.
4. The method of claim 1 wherein the membrane is configured in a corrugated or tortuous flow design to augment turbulence.
5. The method of claim 1 wherein the aqueous brine solution comprises salts
20 selected from the group consisting of seawater, chloride salts, sodium chloride, potassium chloride, calcium chloride, and combinations thereof.
6. The method of claim 1 wherein the recovering step is performed with RO to reconcentrate the aqueous brine solution.
7. a method for treating graywater or filtered blackwater, comprising (a)
25 contacting the graywater or filtered blackwater with one side of a semipermeable membrane, the other side of which is in contact with an aqueous concentrated salt brine solution at a higher osmotic pressure, wherein the graywater or filtered blackwater is provided at a pressure less than 350 kPa, whereby pure water passes through the membrane from the graywater or filtered blackwater into the concentrated salt brine solution to dilute the
30 concentrated salt brine and form a sludge of concentrated graywater or filtered blackwater at less than 5% of its original volume, (b) disposing of the graywater or filtered blackwater sludge, and (c) discarding the diluted salt brine into the ocean.
8. The method of claim 7 wherein the aqueous stream has a fluid velocity across the membrane surface greater than 0.15 m/sec.
- 35 9. The method of claim 7 wherein the membrane is configured in a corrugated or tortuous flow design to augment turbulence.
10. A method for treating landfill leachate, comprising (a) contacting the leachate with one side of a semipermeable membrane, the other side of which is in contact with an

aqueous brine solution at a higher osmotic pressure, wherein the leachate is provided at a pressure less than 350 kPa, whereby pure water from the leachate passes through the membrane into the aqueous brine solution, and (b) recovering pure water from the aqueous brine solution by a reclamation procedure selected from the group consisting of (1) a reverse osmosis (RO) process, (2) an electrodialysis process, (3) an evaporation process, and (4) a combination thereof, thereby reconcentrating the aqueous brine solution.

11. The method of claim 10 wherein the leachate has a fluid velocity across the membrane surface greater than 0.15 m/sec.

12. The method of claim 10 wherein the membrane is configured in a corrugated or tortuous flow design to augment turbulence.

13. The method of claim 10 wherein the landfill leachate is pretreated by a process selected from the group consisting of chemical addition, microfiltration, ultrafiltration, reverse osmosis, and combinations thereof whereby the pretreatment process is able to remove up to 80% of the water in landfill leachate.

14. The method of claim 10 wherein the aqueous brine solution is a concentrated or saturated solution of a chloride salt selected from the group consisting of sodium chloride, potassium chloride, calcium chloride, and combinations thereof.

15. The method of claim 10 wherein the recovering step is performed with RO to reconcentrate the aqueous brine solution.

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Direct Osmosis

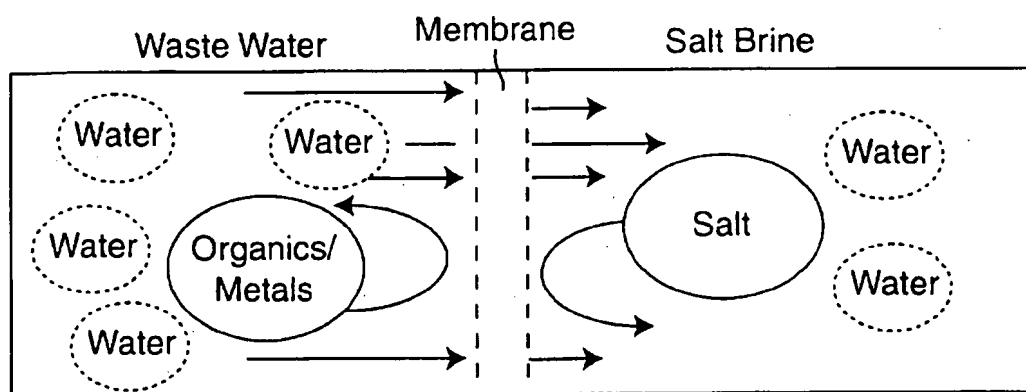


Figure 1

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Flux in Continuous Mode vs. Time

Real Waste Through CTA Into NaCl

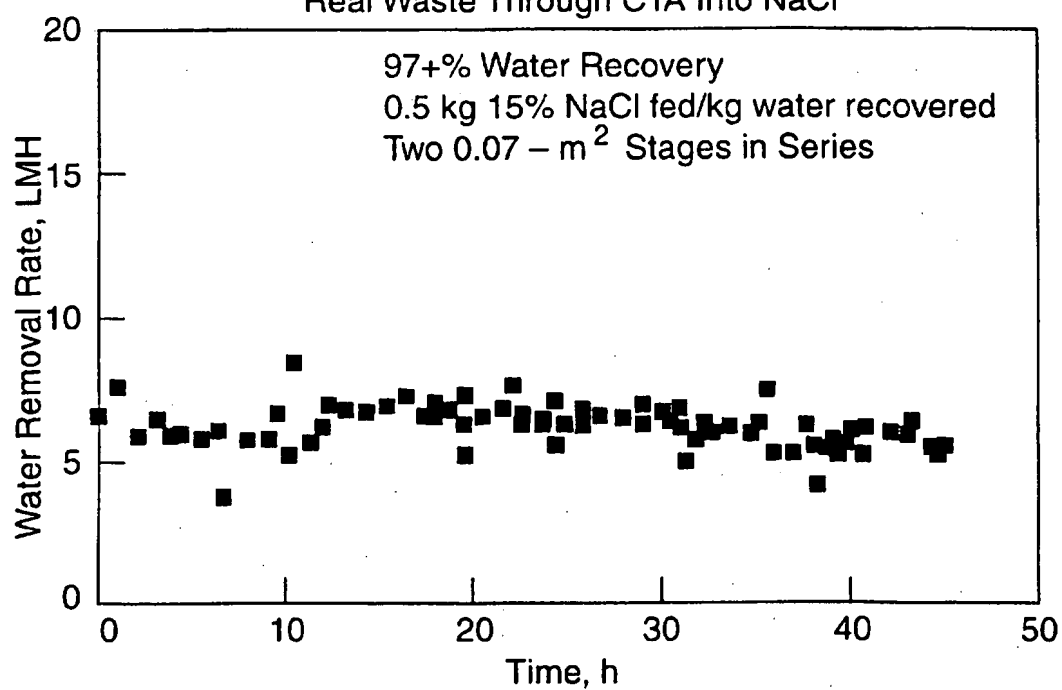


Figure 2

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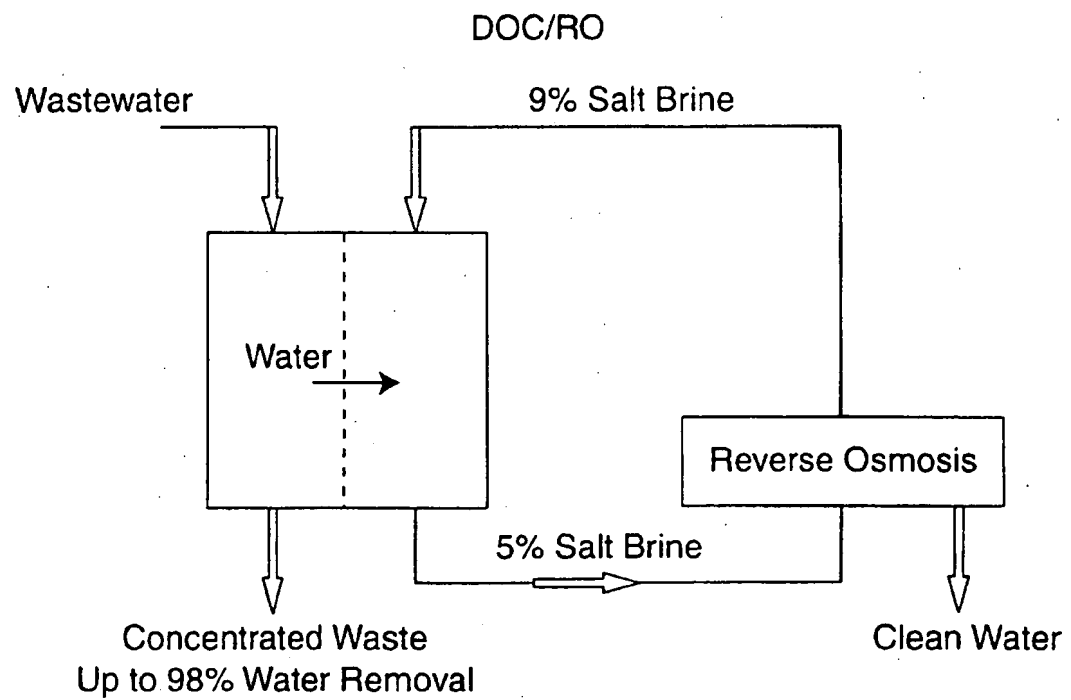


Figure 3

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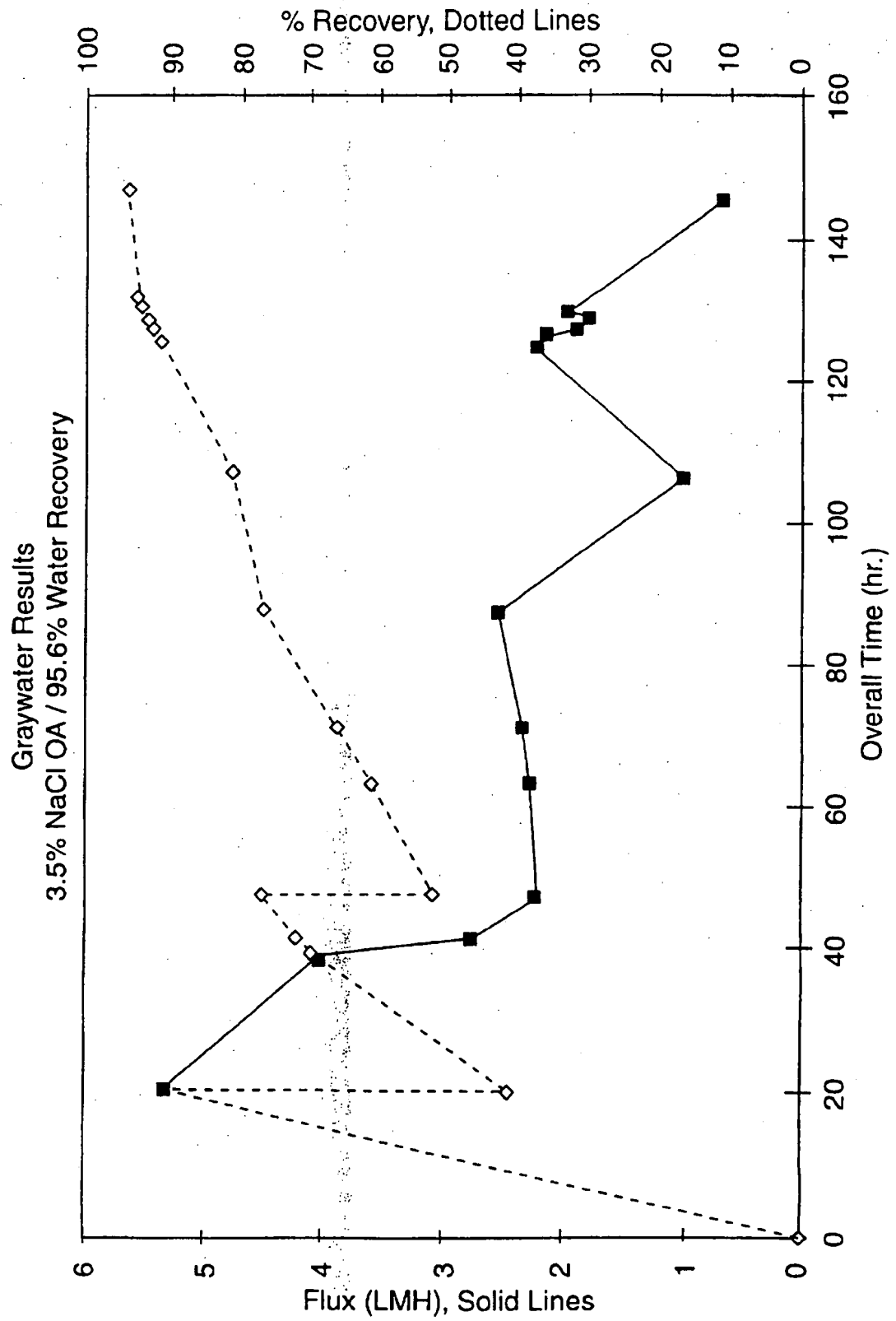


Figure 4

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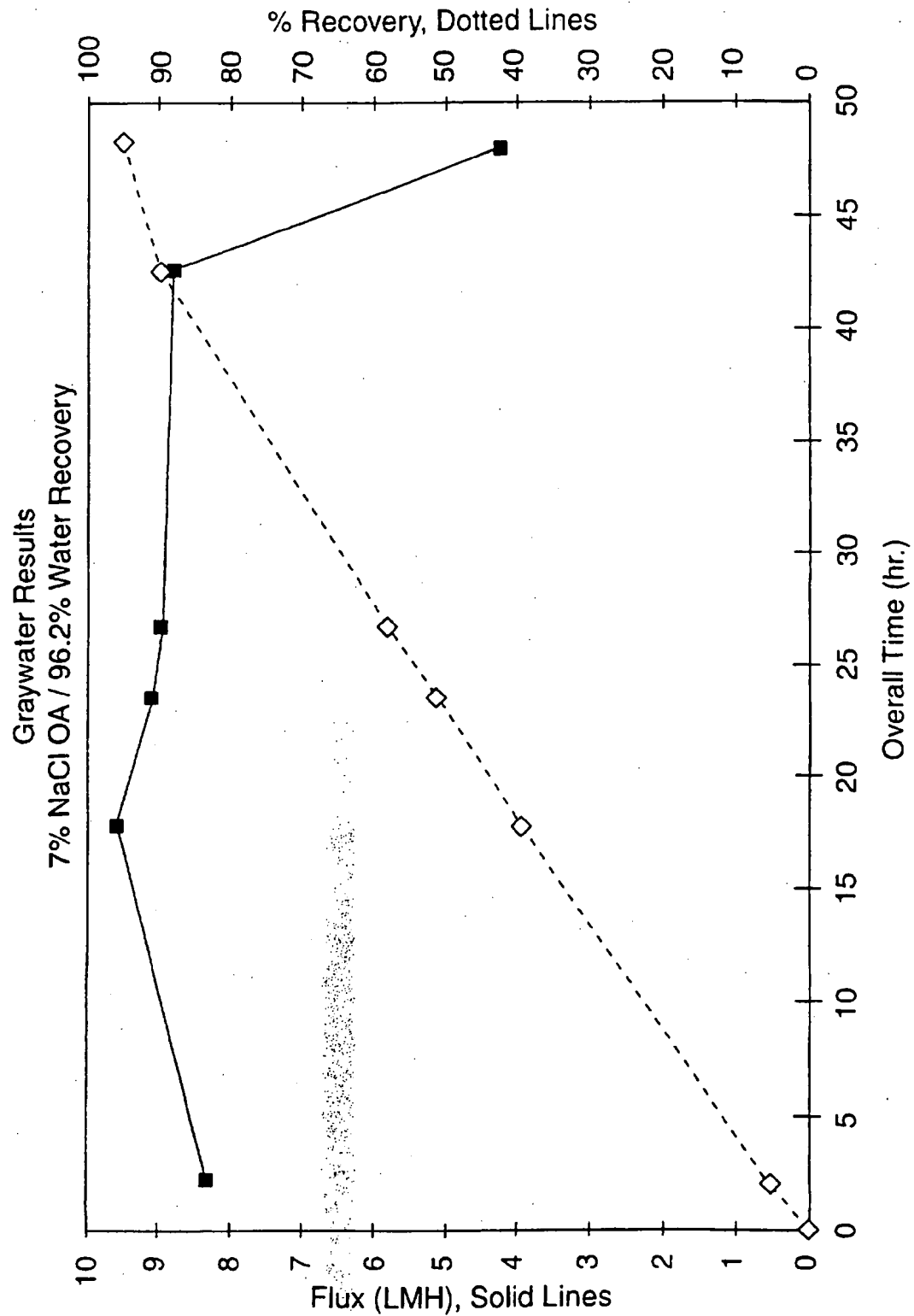


Figure 5

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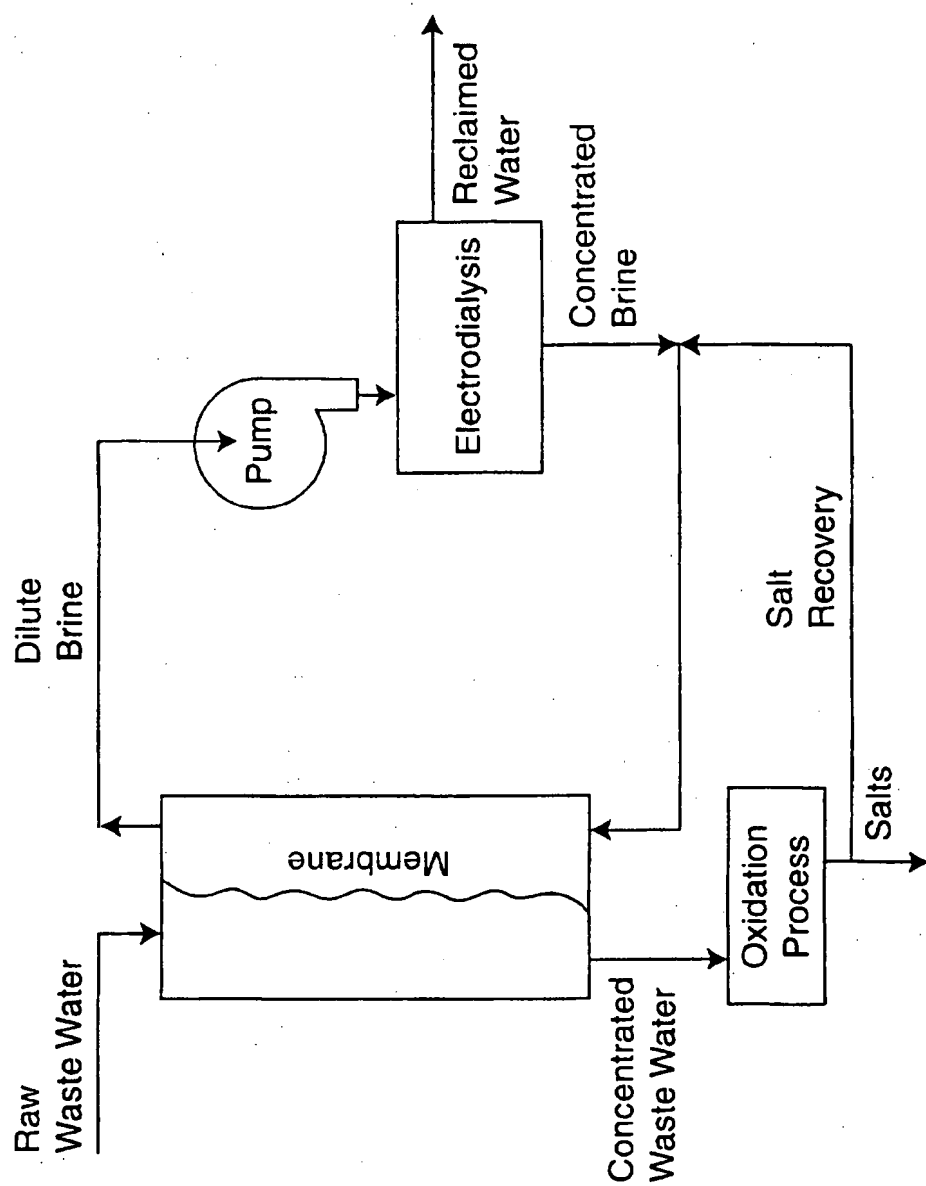


Figure 6

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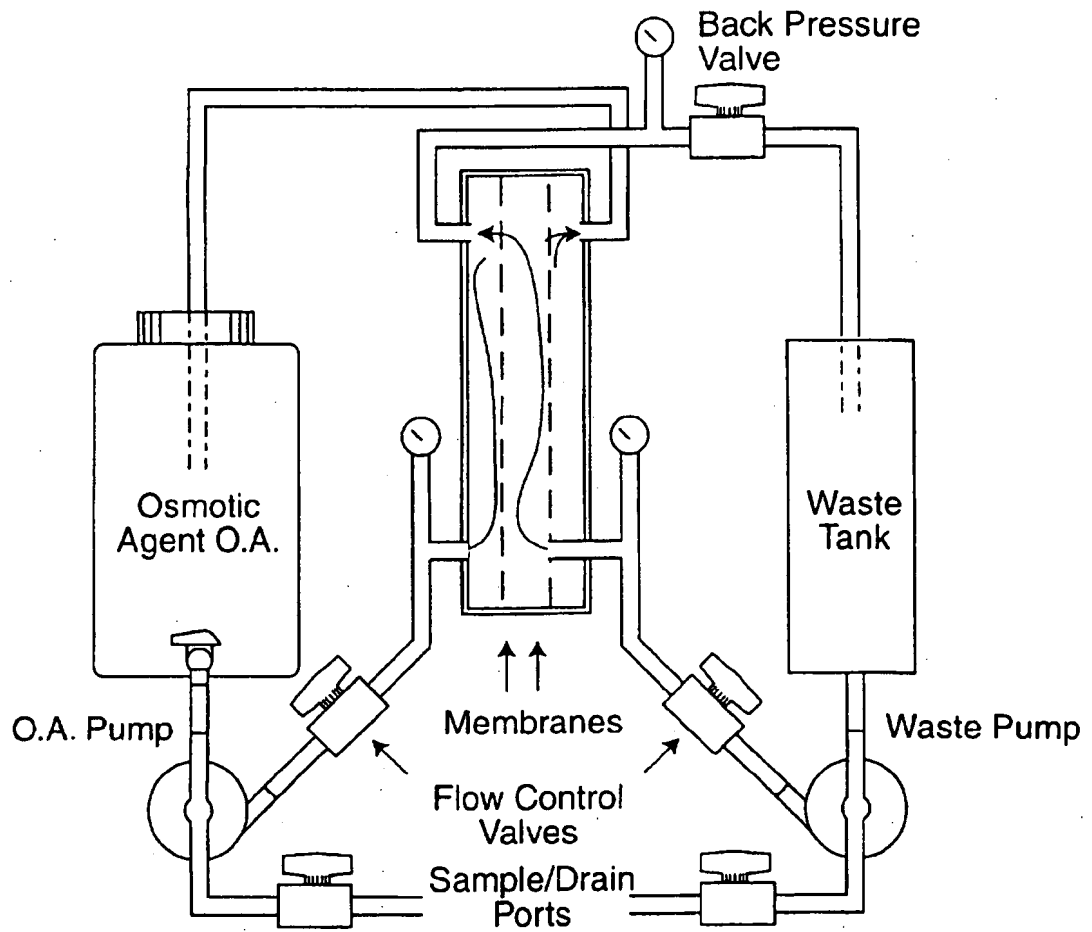


Figure 7

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Water Recovery of 86% From Dilute Ersatz Waste Water

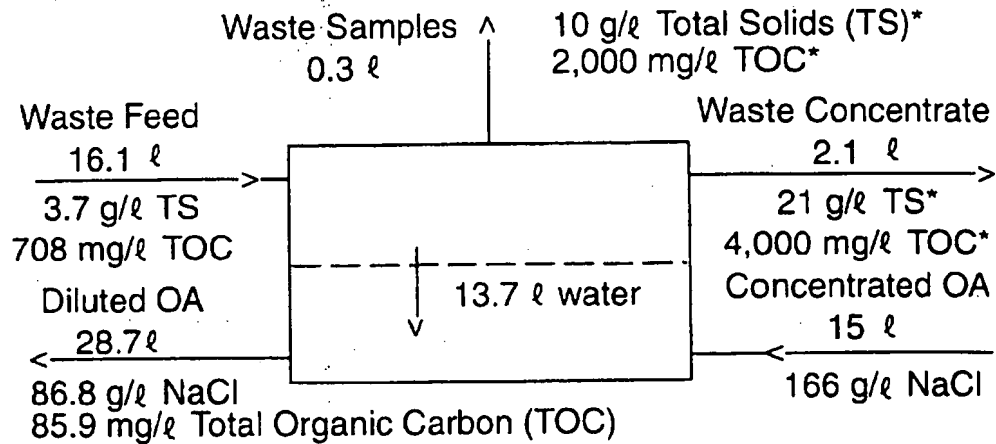
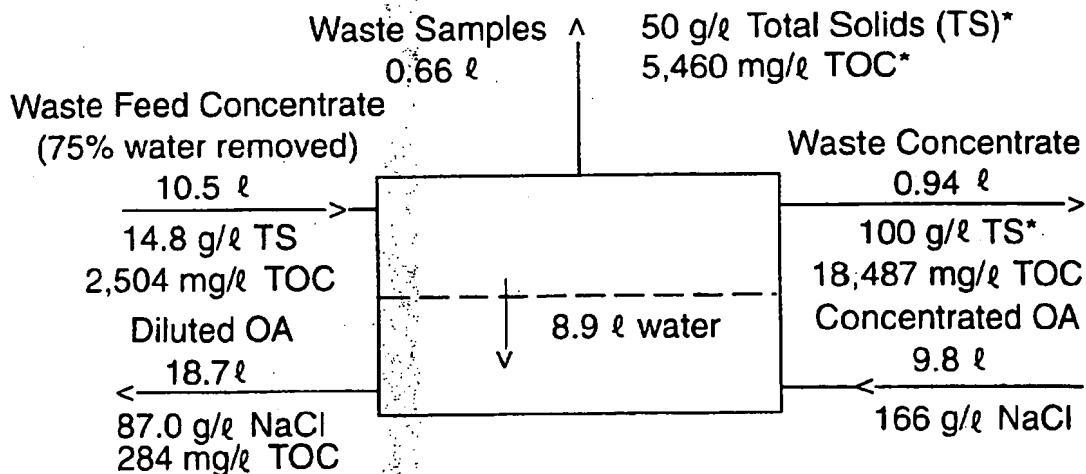


Figure 8a

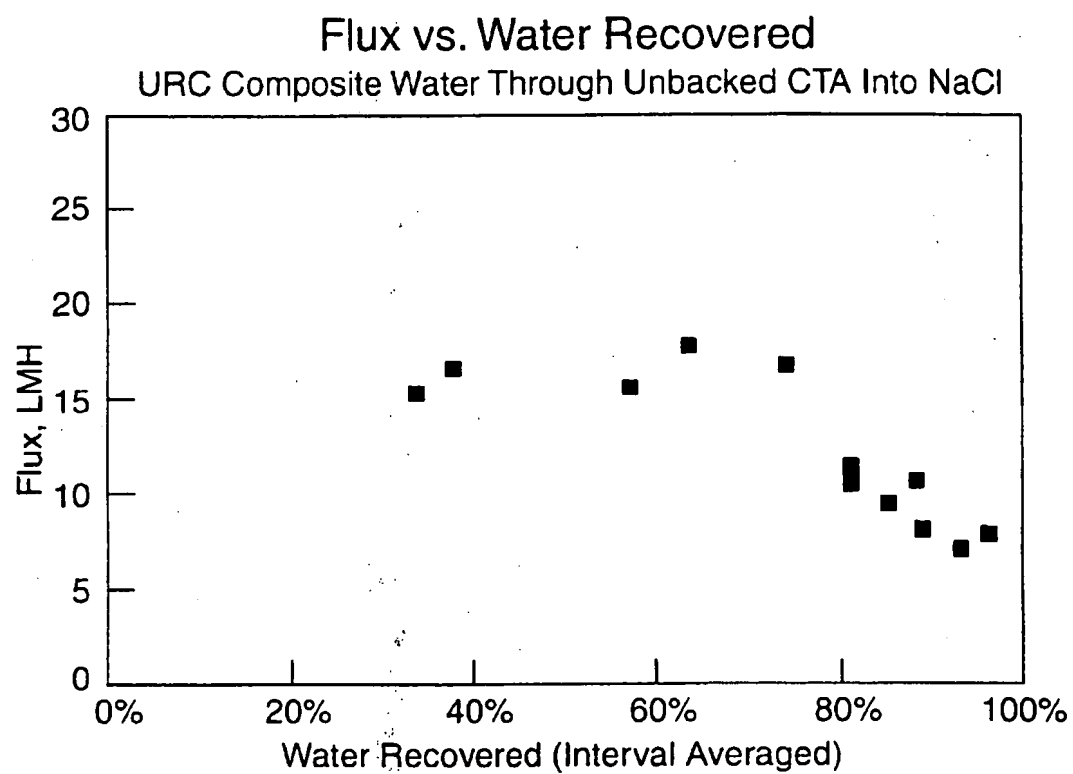
Water Recovery of 97+% From Concentrated Ersatz Waste



*Calculated or estimated values. Assumed organic solids of 5 mg organic solids/mg TOC, which corresponds to urea.

Figure 8b

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**Figure 9**

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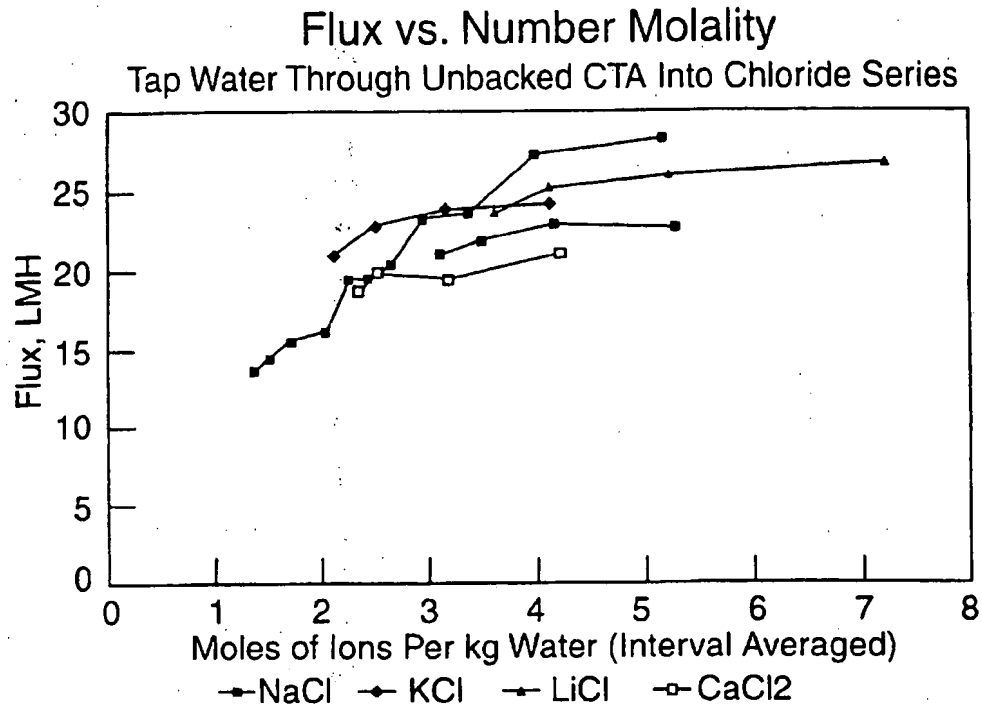


Figure 10a

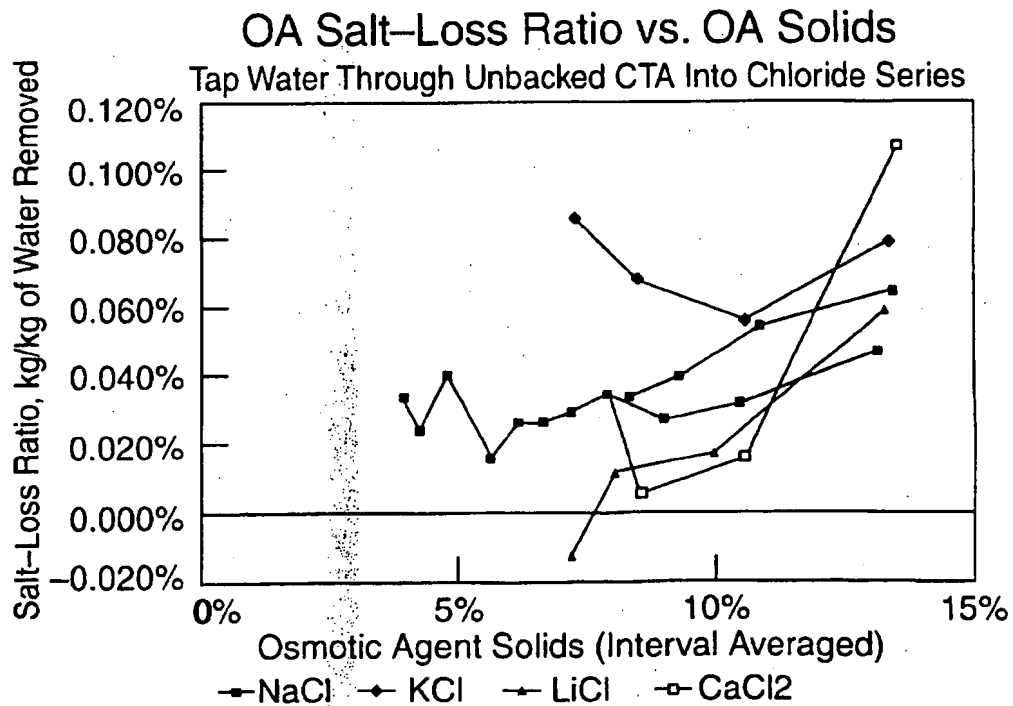


Figure 10b

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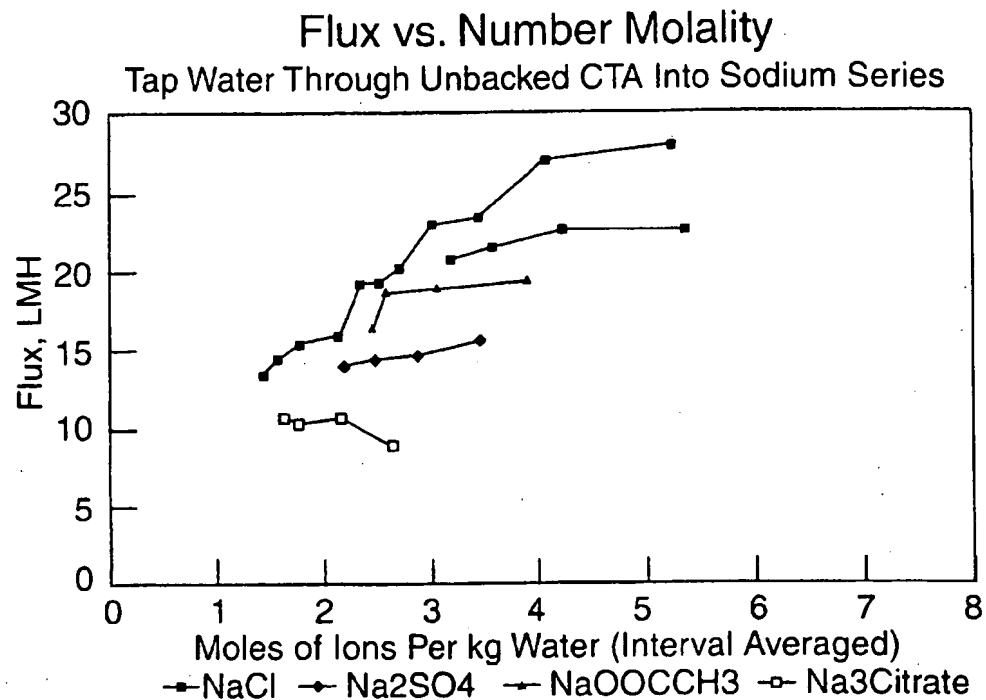


Figure 11a

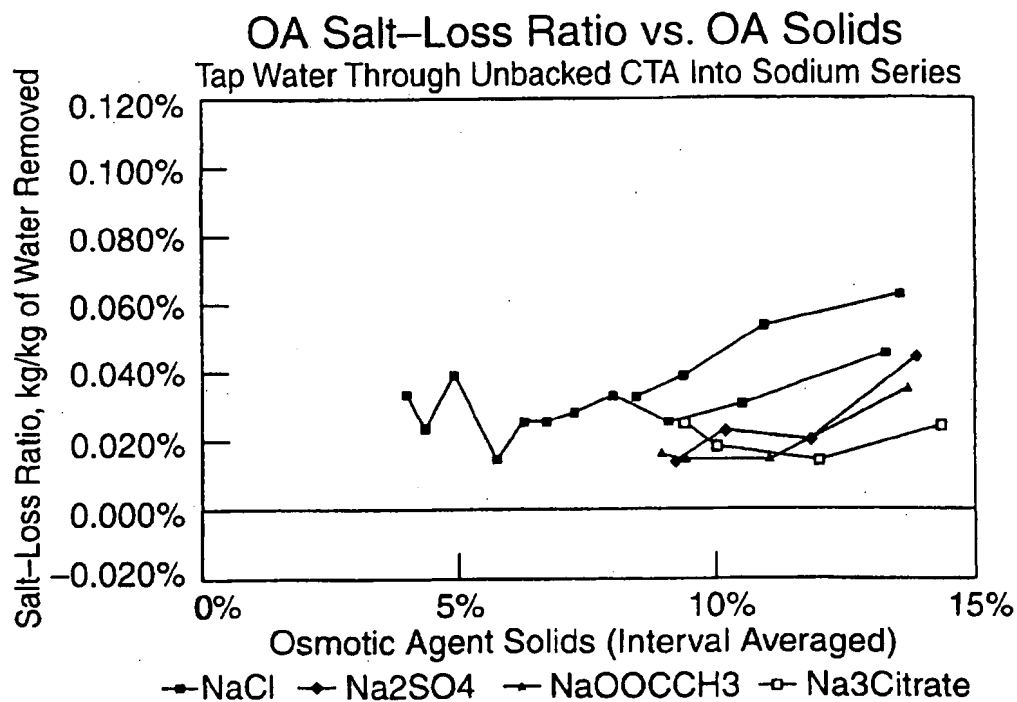


Figure 11b

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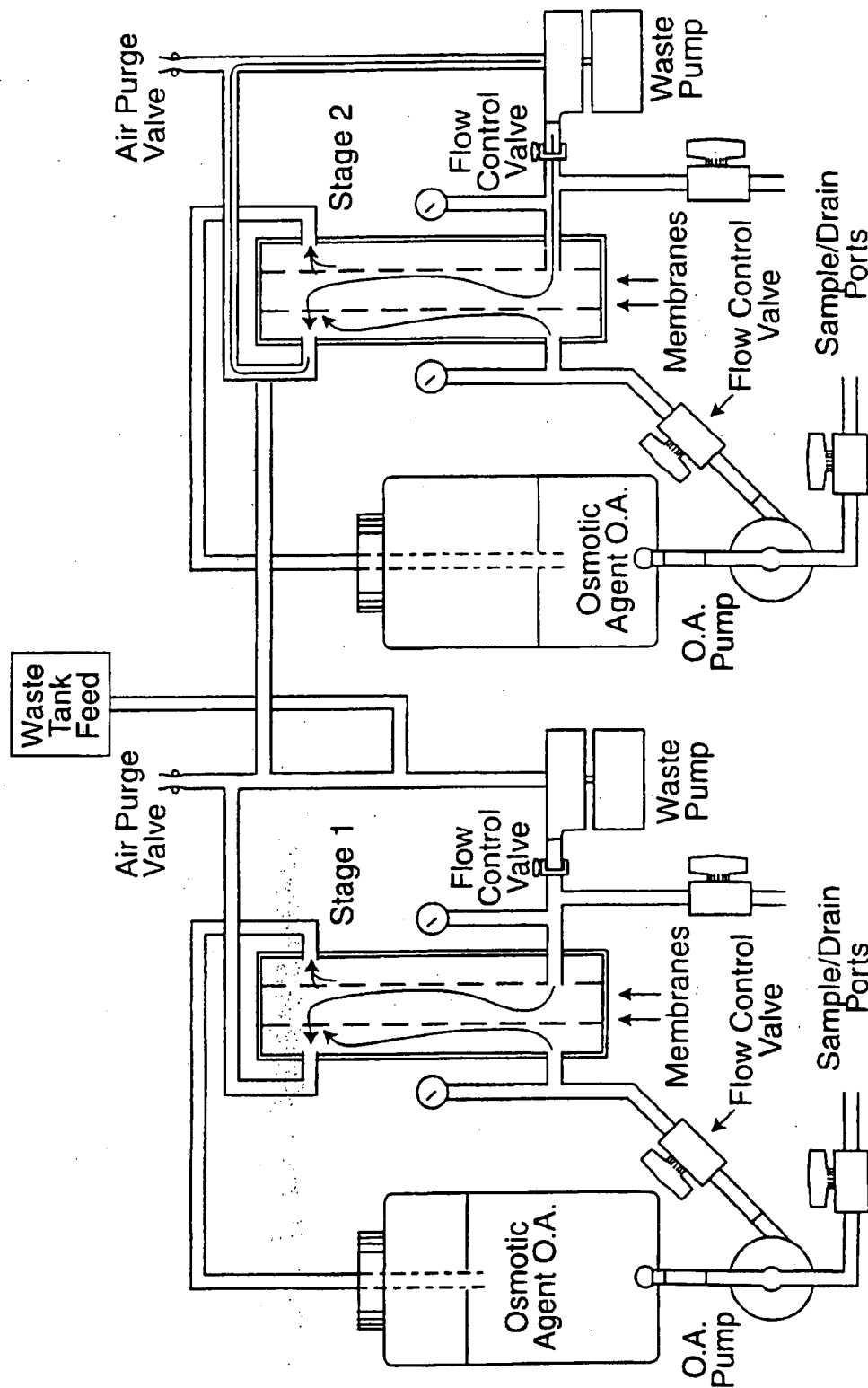
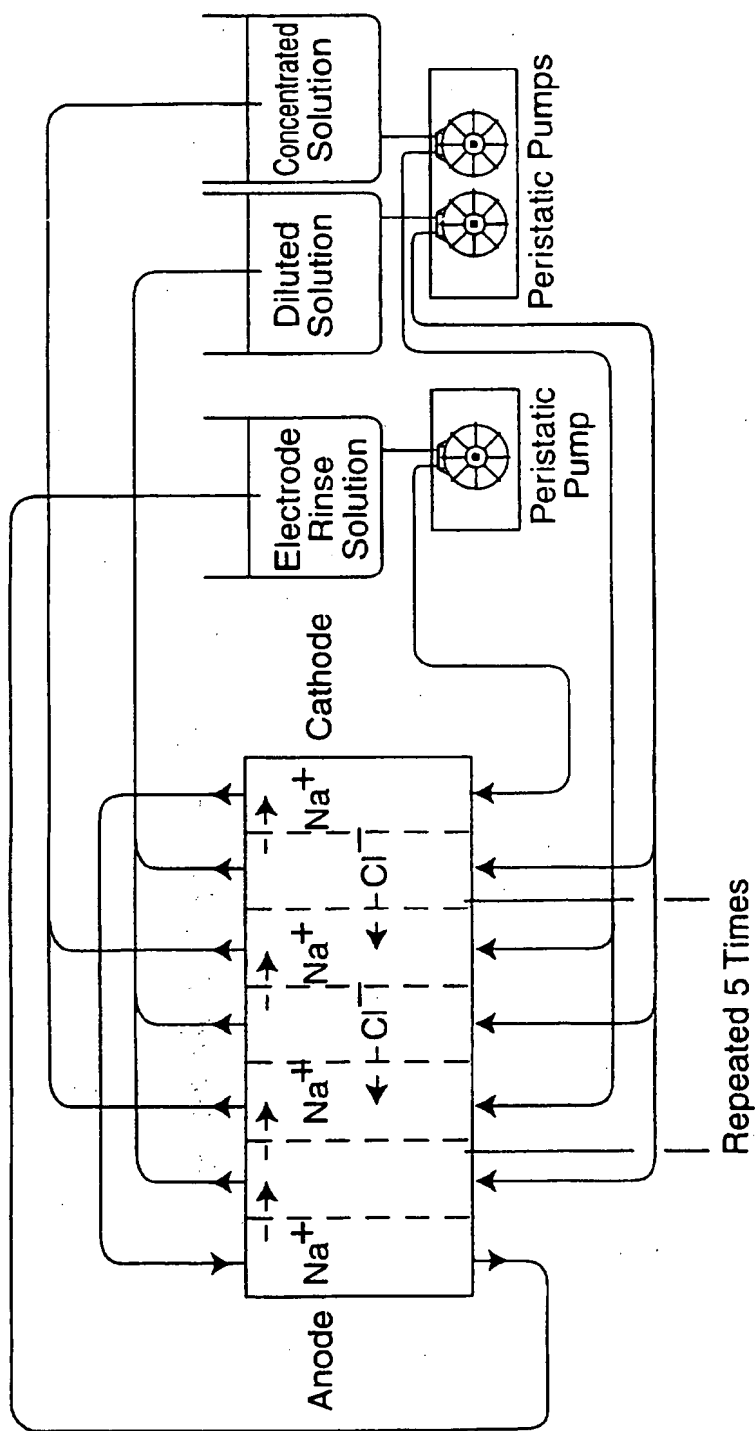


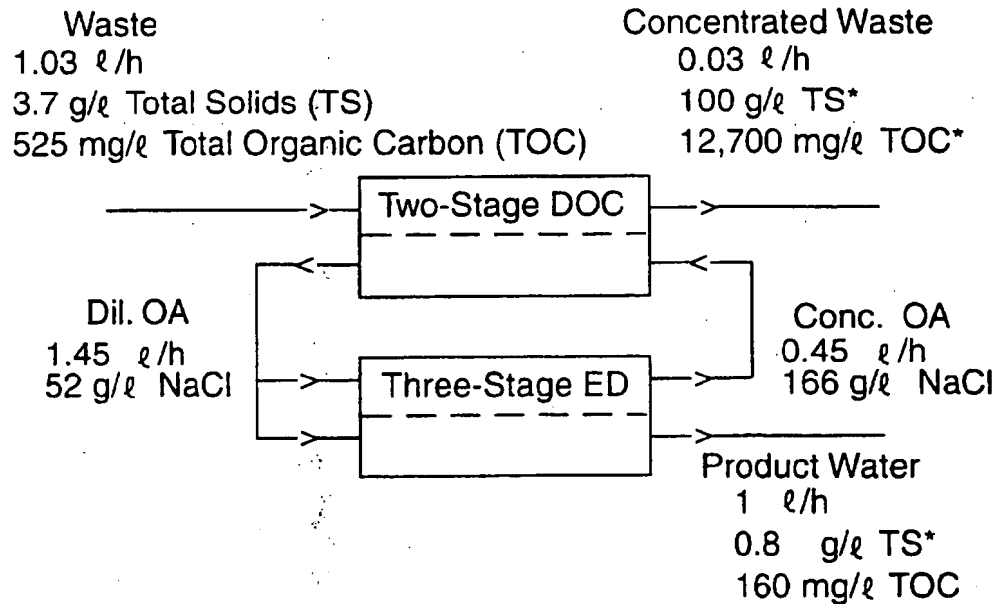
Figure 12

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IONICS Mark 1 Electrolysis Stack
Figure 13

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*Calculated or estimated values. Assumed organic solids of 5 mg organic solids/mg TOC, which corresponds to urea.

Figure 14

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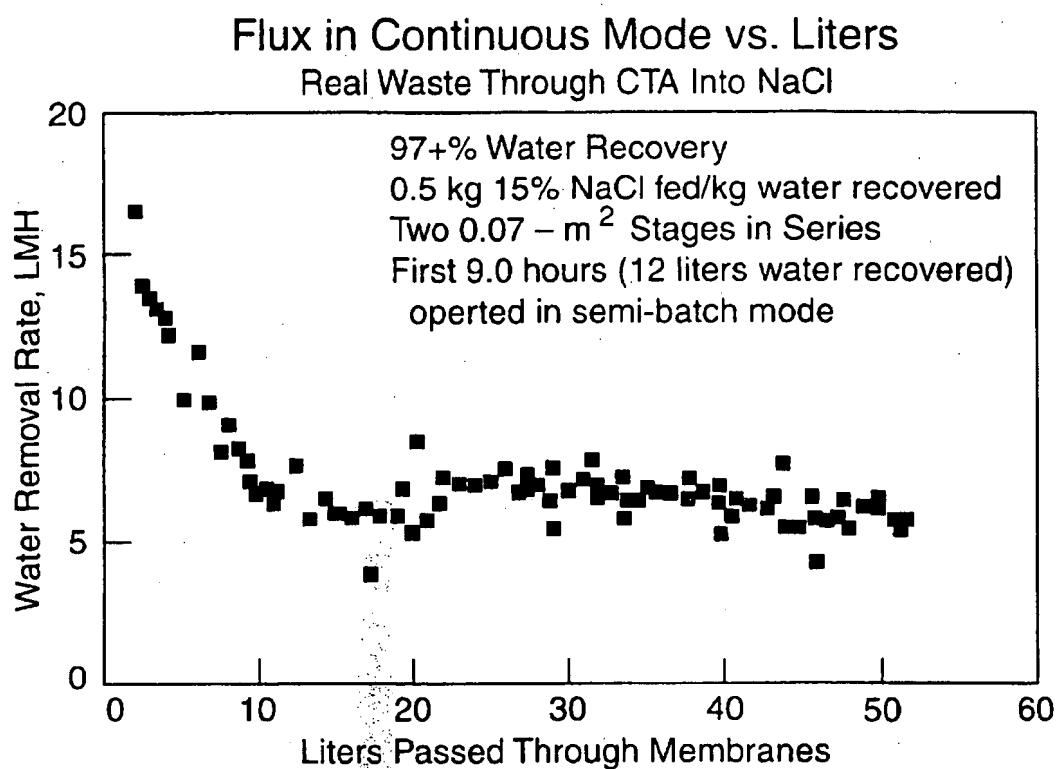
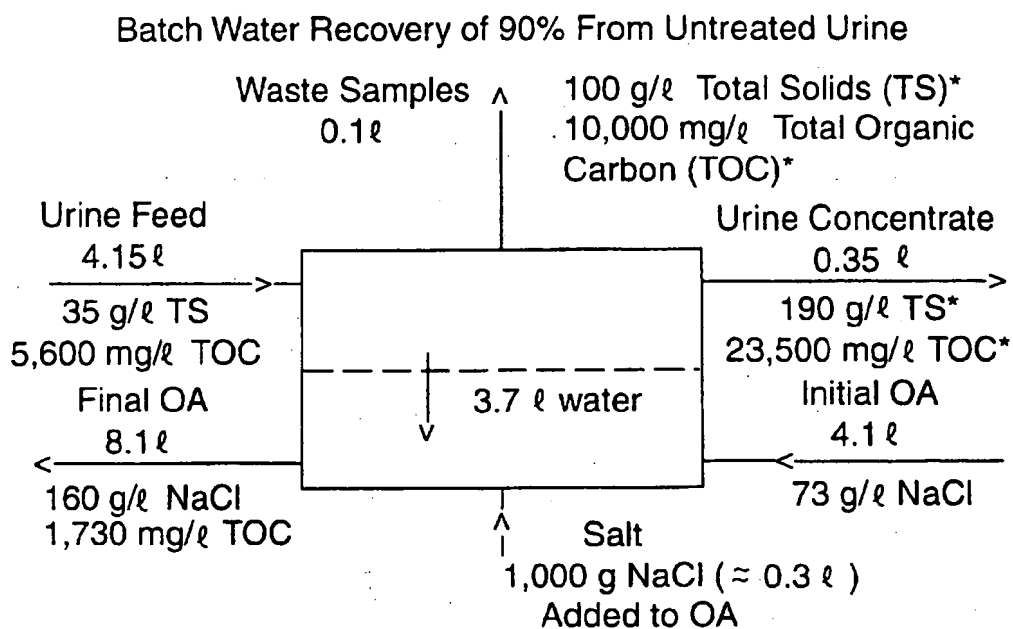


Figure 15

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*Calculated or estimated values. Feed composition was estimated. Assumed organic solids of 5 mg organic solids/mg TOC, which corresponds to urea.

Figure 16

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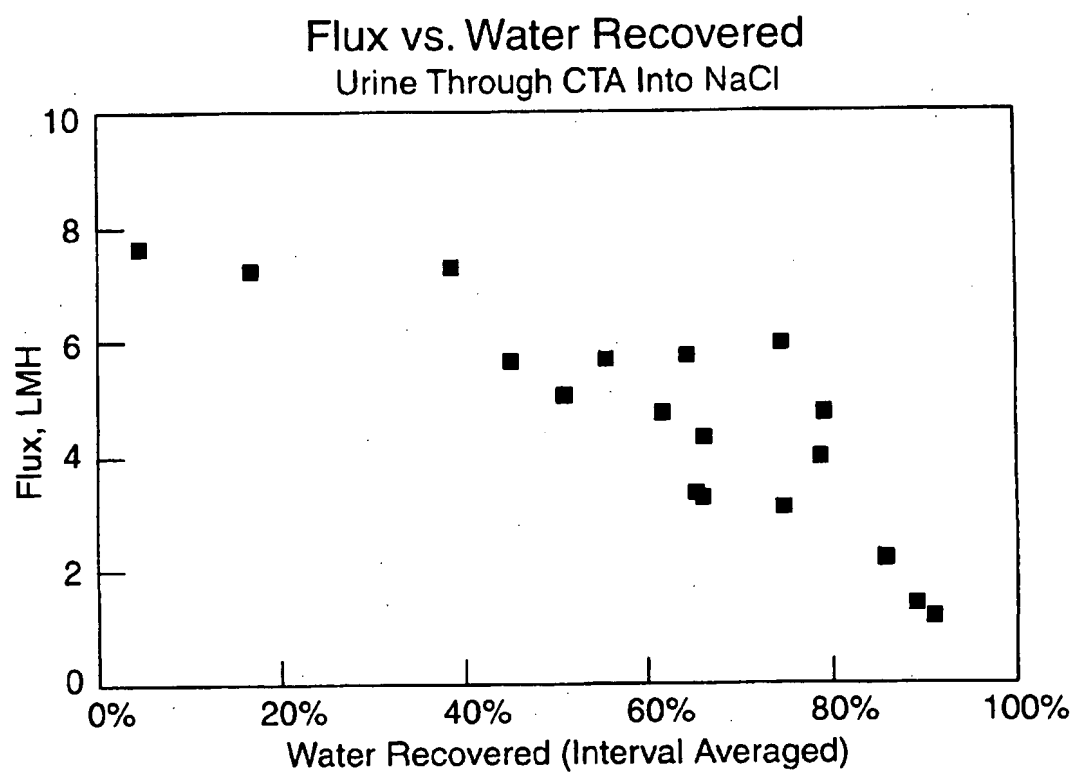


Figure 17